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**Ammonia emissions from pig  
and cattle slurry in the field and  
utilization of slurry nitrogen in  
crop production**

**Doctoral Dissertation**

Pasi K. Mattila

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# Ammonia emissions from pig and cattle slurry in the field and utilization of slurry nitrogen in crop production

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## Abstract

Volatilization of ammonia ( $\text{NH}_3$ ) from animal manure is a major pathway for nitrogen (N) losses that cause eutrophication, acidification, and other environmental hazards. In this study, the effect of alternative techniques of manure treatment (aeration, separation, addition of peat) and application (broadcast spreading, band spreading, injection, incorporation by harrowing) on  $\text{NH}_3$  emissions in the field and on N uptake by ley or cereals was studied. The effect of a mixture of slurry and peat on soil properties was also investigated. The aim of this study was to find ways to improve the utilization of manure N and reduce its release to the environment. Injection into the soil or incorporation by harrowing clearly reduced  $\text{NH}_3$  volatilization from slurry more than did the surface application onto a smaller area by band spreading or reduction of the dry matter of slurry by aeration or separation. Surface application showed low  $\text{NH}_3$  volatilization, when pig slurry was applied to tilled bare clay soil or to spring wheat stands in early growth stages. Apparently, the properties of both slurry and soil enabled the rapid infiltration and absorption of slurry and its ammoniacal N by the soil. On ley, however, surface-applied cattle slurry lost about half of its ammoniacal N. The volatilization of  $\text{NH}_3$  from surface-applied peat manure was slow, but proceeded over a long period of time. After rain or irrigation, the peat manure layer on the soil surface retarded evaporation. Incorporation was less important for the fertilizer effect of peat manure than for pig slurry, but both manures were more effective when incorporated. Peat manure applications increase soil organic matter content and aggregate stability. Stubble mulch tillage hastens the effect in surface soil compared with ploughing. The apparent recovery of ammoniacal manure N in crop yield was higher with injection and incorporation than with surface applications. This was the case for leys as well as for spring cereals, even though  $\text{NH}_3$  losses from manures applied to cereals were relatively low with surface applications as well. The ammoniacal N of surface-applied slurry was obviously adsorbed by the very surface soil and remained mostly unavailable to plant roots in the dry soil. Supplementing manures with inorganic fertilizer N, which adds plant-available N to the soil at the start of growth, increased the overall recovery of applied N in crop yields.

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*Key words: manure, slurry, nitrogen, ammonia, fertilization, peat*

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# Ammoniakkipäästöt sian ja naudan lietelannasta pellolla ja lannan typen hyväksikäyttö kasvintuotannossa

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## Tiivistelmä

Merkittävä määrä typpeä kulkeutuu ympäristöön karjanlannasta haihtuvana ammoniakkina. Ammoniakkipäästöt aiheuttavat rehevöitymistä, happamoitumista ja muita ympäristöhaittoja. Tässä tutkimuksessa selvitettiin erilaisten lannankäsittelytekniikoiden (ilmastus, separointi, imeyttäminen turpeeseen) ja levitystapojen (hajalevitys, nauhalevitys letkulevittimellä, sijoittaminen, multaaminen äestämällä) vaikutusta ammoniakin haihtumiseen pellolla sekä nurmen ja viljojen typenottoon. Myös turpeeseen imeytetyn lietelannan vaikutusta maan ominaisuuksiin tutkittiin. Tavoitteena oli löytää menetelmiä, joilla voidaan lisätä lannan typen hyväksikäyttöä ja vähentää typpipäästöjä ympäristöön. Sijoittaminen ja multaaminen äestämällä vähensivät ammoniakin haihtumista selvästi enemmän kuin lannan levittäminen pienemmälle alalle nauhalevityksen avulla tai lannan kuiva-aineen vähentäminen ilmastuksella tai separoinnilla. Pintalevityksen ammoniakkipäästöt olivat pienet, kun sian lietelantaa levitettiin muokatulle savimaalle tai kevätkuivakasvustoon varhaisissa kasvuvaiheissa. Nurmella sen sijaan pintalevitetyn naudan lietelannan liukoisesta tyypestä haihtui noin puolet. Pintalevitetystä turvelannasta ammoniakin haihtuminen oli hidasta mutta jatkui pitkään. Sateen tai sadetuk- sen jälkeen turvelantakerros maan pinnalla hidasti maan kuivumista. Multaaminen oli turvelannan typen hyväksikäytön kannalta vähemmän tärkeää kuin lietelannan, mutta kumpikin lanta vaikutti voimakkaammin mullattuna. Toistuvasti käytettynä turvelanta lisää maan eloperäistä ainesta ja murujen kestävyyttä. Sänkimuokkaus nopeuttaa vaikutusta pintamaassa kyntöön verrattuna. Sijoittaminen ja multaaminen nostivat lannan liukoisen typen näennäistä hyväksikäyttöastetta sekä nurmella että viljoilla, vaikka viljapellosta ammoniakin haihtuminen oli vähäistä myös lannan jäädessä pintaan. Viljapeltoon pintalevitetyn lannan liukoinen tyyppi ilmeisesti sitoutui kuivaan pinta- maahan ja oli pääosin kasvien juurten ulottumattomissa. Karjanlannan täy- dentäminen väkilannoitetyypellä, mikä lisää kasveille käyttökelpoisen typen määrää maassa kasvukauden alussa, kohotti lannan ja väkilannoitteen typen näennäistä hyväksikäyttöastetta.

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*Avainsanat: karjanlanta, lietelanta, tyyppi, ammoniakki, lannoitus, turve*

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## Foreword

The studies presented in this thesis were conducted at the Soils and Environment unit of Agrifood Research Finland and at the Department of Applied Chemistry and Microbiology of the University of Helsinki in 1990–2000. The field experiments were carried out in Jokioinen, Ruukki and Vihti. The laboratory work of ammonia measurements and soil and crop analysis was performed in Jokioinen.

The research was initiated by the late Professor Paavo Elonen to whom I am grateful for leading me into research work with field experiments. I thank Professor Antti Jaakkola for his guidance in my studies and for his helpful comments on the manuscript. Professor Martti Esala offered valuable proposals for improvements on this thesis. Professor Markku Yli-Halla contributed greatly to shaping the work to its final form. I am grateful to Petri Kapuinen, Lic.Sc.Agric., Erkki Joki-Tokola, M.Sc.Agric. and Mr. Risto Tanni for their excellent co-operation and productive discussions in conducting the experiments and in publishing the results. I gratefully acknowledge Professor Raimo Kõlli and Professor Sven G. Sommer for their insightful pre-examination of the manuscript. Several people were involved in the field and laboratory work of the experiments. I wish to thank them all for their excellent work. I am especially grateful to Ms. Leena Mäkäraäinen, who developed special skills in the management of ammonia samplers.

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Helsinki, October 2006

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## Original publications

- I Mattila, P.K. & Joki-Tokola, E. 2003. Effect of treatment and application technique of cattle slurry on its utilization by ley: I. Slurry properties and ammonia volatilization. *Nutrient Cycling in Agroecosystems* 65: 221–230.
- II Mattila, P.K., Joki-Tokola, E. & Tanni, R. 2003. Effect of treatment and application technique of cattle slurry on its utilization by ley: II. Recovery of nitrogen and composition of herbage yield. *Nutrient Cycling in Agroecosystems* 65: 231–242.
- III Mattila, P.K. & Kapuinen, P. Ammonia volatilization from pig slurry applied to spring wheat by different techniques. Submitted to *Bioresource Technology*.
- IV Mattila, P.K. 2006. Spring barley yield and nitrogen recovery after application of peat manure and pig slurry. *Agricultural and Food Science* 15: 124–137.
- V Mattila, P.K. 2006. Ammonia volatilization, nitrogen in soil, and growth of barley after application of peat manure and pig slurry. *Agricultural and Food Science* 15: 138–151.

### The author's contribution in joint publications

- I Pasi Mattila planned and conducted the ammonia measurements, calculated and interpreted their results, and was mainly responsible for writing the paper.
- II Pasi Mattila participated in the management of the field experiment in Jokioinen, and participated in the calculation and interpretation of the results of both Jokioinen and Ruukki, and was mainly responsible for writing the paper.
- III Pasi Mattila planned and conducted the ammonia measurements, calculated and interpreted their results, and was mainly responsible for writing the paper.

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# 1 Introduction

## 1.1 The development of manure into an environmental problem

The availability of nitrogen (N) limits crop growth in most agroecosystems, which makes it necessary to supply N by fertilization. Until the 20<sup>th</sup> century, animal manure was the primary N fertilizer in agriculture in Finland and other parts of Europe (SKS 2003, Krausmann 2004). The production of manure was an essential motive for farmers to raise animals. Feed for cattle was gathered from large natural areas, and their manure was collected and used as a fertilizer in farmed fields. This way N and other nutrients could be concentrated on the relatively small field area close to human dwellings. Animals converted the nutrients of plant material into a form more available for crops. The nutrients of cultivated crops used as animal feed were recycled back into crop production through manure application.

The industrial fixation of atmospheric N to produce inorganic fertilizers changed the situation remarkably during the 20<sup>th</sup> century (SKS 2003, Krausmann 2004, SKS 2004). It was now possible to apply large amounts of plant-available N to agricultural land. The supply of N to crops increased significantly and the dependence on manure as a source of N decreased. Fodder crops were increasingly grown on farmed grassland or on arable land, and the use of natural areas diminished. Animal feed became more concentrated with nutrients and, consequently, the nutrient content of animal manure increased. Thus, manure became a more effective fertilizer and its production increased with the number of farm animals, but industrial fertilizers rendered manure less important as a source of nutrients in crop production. Manure increasingly became a waste to be disposed of by application to fields. Effective utilization of manure N and other nutrients by crops was not important. In many cases, the amounts of nutrients contained in manure far exceeded the demand of the crops. Unfavourable timing and techniques of manure application were other factors contributing to low utilization of manure nutrients. Consequently, large amounts of nutrients were dispersed into the environment with negative results, such as the eutrophication of natural habitats, nitrate ( $\text{NO}_3^-$ ) contamination of groundwater, and soil acidification (van der Hoek 1998, Galloway et al. 2003).

Environmental pollution and increases in production costs of industrial N fertilizers during the energy crisis of the 1970s led to efforts to improve the utilization of manure N (SITRA 1970, Uomala 1986). However, a large part of manure N remains lost into the environment. Losses occur in all stages of manure handling, but the largest emissions occur through the volatilization of ammonia ( $\text{NH}_3$ ) from field-applied manure (Bussink and Oenema 1998). N may also be lost through gaseous emissions from nitrification and denitrifica-

tion (Rubæk et al. 1996), the leaching of N (Kemppainen 1995), and the volatilization of  $\text{NH}_3$  from plants (Mattson et al. 1998).

Dairy and beef cattle produce about 80%, and pigs about 14%, of the total amount of manure in Finland (Kapuinen 1994). Other domestic animals are of minor importance as sources of manure, although poultry and fur animals, for example, are locally significant. Changes in the number of domestic animals, such as the decline in the number of dairy cattle (TIKE 2004), have probably affected the amount of manure. Most of the manure from cattle and sows is still treated in solid form with added bedding (Seppänen and Matinlassi 1998, Pyykkönen et al. 2004), but the proportion of slurry is increasing with the shift from small and old animal buildings to larger units (Kapuinen 1994). For fattening pigs, slurry is already the most common form of manure. In the late 1990's, 60% of cattle and pig manure was applied in spring and 35% in autumn (Seppänen and Matinlassi 1998). Application to growing crops in summer is increasing, because the implementation of the European Union's  $\text{NO}_3^-$  directive (VNa 931/2000) and Finland's agri-environmental program (MMMa 646/2000) restrict manure spreading in autumn. Winter application of manure is totally banned. Furthermore, the increasing use of new manure application techniques, such as band spreaders and injectors, facilitates the application of manure into growing crops. Even though the effective utilization of manure nutrients is often more expensive and more laborious than the use of inorganic fertilizers (Araji et al. 2001, Huijsmans et al. 2004), manure should be managed so that the losses of nutrients to the environment are minimized and nutrients are cycled within agriculture.

## 1.2 N in manure

The manure of domestic animals consists of urine and faeces and other material entering the manure (e.g. bedding materials, remains of feed and washing water). The composition of manure varies because of different physiologies and feeding practices for domestic animals, and methods of handling and storing the manure (Table 1). Cattle and pigs excrete surplus N as urea in urine. In poultry faeces, the corresponding compound is uric acid. Excessive N in diet results in higher N concentrations in urine and, consequently, in manure (Misselbrook et al. 2005a, Nennich et al. 2005, Velthof et al. 2005). Urea and uric acid are hydrolysed to ammoniacal N (Whitehead and Raistrick 1993), which is the most important source of readily plant-available N in manure. N is also contained in the organic matter of manure, which originates mainly from faeces and bedding materials. Organic N can become plant-available through mineralization by organisms that decompose organic matter. However, such decomposition may reduce plant-available N through the immobilization of N into organic matter, especially if easily decomposable material with a high ratio of carbon to N (C/N), such as straw, is added to the manure (Meyer and Sticher 1983, Sørensen 1998).

Table 1. Average properties of cattle and pig manure in Finland (Kemppainen 1989, p. 177).

Animal	Manure	Dry matter %	pH	Total N	Ammoniacal N			Ammoniacal N / Total N
					P	K	%	
g/kg								
Cattle	Solid	18.4	7.1	4.6	1.2	1.6	4.2	26
	Slurry	8.1	7.0	3.3	1.8	1.0	2.8	56
	Urine	2.6	8.0	3.1	2.8	0.2	5.0	87
Pig	Solid	23.0	7.1	7.2	2.8	3.7	4.0	37
	Slurry	9.2	7.0	5.4	3.6	1.9	2.0	70
	Urine	1.8	7.6	2.6	2.2	0.5	1.4	86

## 1.3 NH<sub>3</sub> emissions from manure

### 1.3.1 Sources of NH<sub>3</sub>

NH<sub>3</sub> volatilization is a major pathway of N emissions to the air and of subsequent N deposition, whereas agriculture is the main source of NH<sub>3</sub> emissions. Olivier et al. (1998) estimated that about 70% of global NH<sub>3</sub> emission is related to food production. The main source of agricultural NH<sub>3</sub> emissions is the manure of farm animals. Farm animals and manure in different stages of manure treatment account for 74% of all anthropogenic NH<sub>3</sub> emissions in Western Europe, whereas fertilizer application and crops produce 18% of the emissions (ECETOC 1994). In Western Europe, 25% of the N excreted by farm animals is lost through NH<sub>3</sub> emissions, and 43% of the emissions occur after manure application in the field (ECETOC 1994). In Finland, the share of manure is estimated at 84% of total NH<sub>3</sub> emission (Grönroos et al. 1998). The distribution of NH<sub>3</sub> emissions in the various stages of slurry treatment is different from that of solid manure (Table 2). Most of the NH<sub>3</sub> volatilization from slurry occurs after application in the field, whereas emissions from solid manure are highest during storage.

National and international measures have been undertaken to reduce NH<sub>3</sub> emissions. NH<sub>3</sub> is included in the United Nations' Convention on long-range transboundary air pollution (UN 2004) and in the National Emission Ceilings Directive of the European Union (EC 2001), which set national limits to NH<sub>3</sub> emissions. For Finland, the NH<sub>3</sub> emission ceiling in 2010 is 31 000 Mg, which requires some reduction compared with the emissions of 33 300 Mg in 2004 (SYKE 2006a). Despite reduction efforts, NH<sub>3</sub> emissions in Europe are expected to remain in present level, and NH<sub>3</sub> will be the main source of N deposition and acidification in the future (Amann et al. 2005).

Table 2. Loss of manure N through NH<sub>3</sub> volatilization (% of initial manure N) at different stages of manure treatment (Grönroos et al. 1998).

	Slurry	Solid manure
Animal buildings	9	18
Manure storage	8	29
Application	16	7
Total	33	54

### 1.3.2 Properties of NH<sub>3</sub>

NH<sub>3</sub> is a colourless gas with a pungent odour. It is a weak base and, hence, its reaction with water raises pH and produces ammonium (NH<sub>4</sub><sup>+</sup>) ions (Figure 1). The N of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> is referred to as ammoniacal N. NH<sub>3</sub> gas dissolves readily into water, but a rise in temperature strongly reduces its solubility (Table 3). Dissolution into water and reaction with water are reversible processes, which move in either direction according to conditions. A rise in pH and temperature results in a shift from NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub>, thus increasing the proportion of NH<sub>3</sub> and also reducing its solubility into water. Together, these processes increase the partial pressure of NH<sub>3</sub> in water and enhance the volatilization of NH<sub>3</sub> into air (Génermont and Cellier 1997).

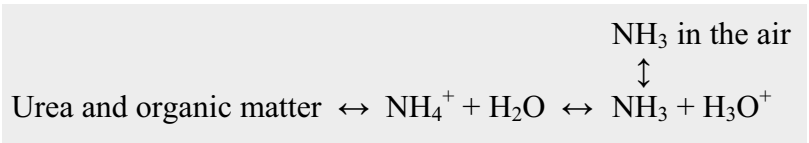


Figure 1. Reactions of the ammoniacal N of manure.

Table 3. Properties of NH<sub>3</sub> (CRC 1984).

Base constant (pK <sub>b</sub> ) at 20°C	4.767
Boiling point	−33.35°C
Solubility: cold water	89.9 g/100 ml
hot water	7.4 g/100 ml

### 1.3.3 Transport and deposition of volatilized NH<sub>3</sub>

In Europe, annual depositions of ammoniacal N as high as almost 20 kg ha<sup>−1</sup> have been estimated for some areas (Holland et al. 2005). In Finland, the

annual ammoniacal N deposition varies from 2–3 kg ha<sup>-1</sup> in the western and southern part of the country to <1 kg ha<sup>-1</sup> in the north (SYKE 2006b). A substantial part of emitted NH<sub>3</sub> is deposited close to the source (Ferm 1998). Deposition is, thus, highest in areas with high emissions, such as agricultural regions with intensive animal production. Large NH<sub>3</sub> concentration and N deposition have been observed at woodland boundaries close to livestock buildings in the prevailing direction of the wind (De Schrijver et al. 1998, Pitcairn et al. 1998), where the forest edge catches the NH<sub>3</sub> transported by air flow over open land. However, significant amounts of volatilized NH<sub>3</sub> can drift hundreds of kilometres (Ferm 1998, van der Hoek 1998). In the atmosphere, sulphuric acid, NH<sub>3</sub>, and water form aerosol particles, which can move long distances and develop into cloud condensation nuclei, thus influencing cloud formation and the global radiation balance (Kulmala et al. 2000). The NH<sub>4</sub><sup>+</sup> containing aerosols contribute to air pollution through particulate matter (EPA 2004), which causes adverse health effects (Katsouyanni et al. 1997, McCubbin et al. 2002). Atmospheric NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> salts are deposited mainly as wet deposition in rain water, but also partially as dry deposition (Ferm 1998, Holland et al. 2005). The distribution of deposition at different distances from the emission source varies according to weather conditions and is difficult to predict.

#### **1.3.4 Effects of deposited NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> in the environment**

NH<sub>3</sub> is an important factor in soil acidification (van Breemen et al. 1982). Nitrification of deposited NH<sub>4</sub><sup>+</sup> releases protons, which lowers soil pH and increases the mobility of aluminium (Egli and Fitze 1995, De Schrijver et al. 1998). In Finland, the critical load of acidifying deposition is exceeded in about half of the county (SYKE 2006c), which means that in this area, detrimental acidification will occur if the deposition is not reduced. However, Tamminen and Derome (2005) found no clear relationship between acid deposition and long-term changes in the properties of Finnish forest soils.

Nitrification of NH<sub>4</sub><sup>+</sup> may be followed by denitrification, which produces dinitrogen oxide (N<sub>2</sub>O) emissions (Böckman and Olf 1998). N<sub>2</sub>O contributes to the warming of the atmosphere (i.e. greenhouse effect) (IPCC 2001) and to the destruction of the stratospheric ozone layer (Crutzen 1970). Increased soil NO<sub>3</sub><sup>-</sup> increases the risk for the leaching of NO<sub>3</sub><sup>-</sup> into ground water (Nissinen and Hari 1998).

Needle analyses have identified high N concentrations in European forests near agricultural areas and increased N availability for trees (Kuylenstierna et al. 1998), which can have adverse effects on forest ecosystems (Schulze et al. 1989, Luyssaert et al. 2003). Deposited N may increase N leaching from forest soil as well as the growth rate of trees, if other nutrients do not limit it (Nissinen and Hari 1998). In the long run, however, N deposition and subse-

quent acidification retard growth in forests with low critical loads of acidity (Nellemann and Thomsen 2001). Increased N concentration changes the composition of plant species favouring species with high N demand over those adapted to low N environments (Pitcairn et al. 1998). N deposition also promotes the expansion of green algae on conifers (Poikolainen et al. 1998). In Finland, however, coniferous forests of southern Finland are not at risk for N saturation, with the present rate of N deposition (Tamminen and Derome 2005).

Part of deposited N ends up in rivers, lakes, and seas either directly or by leaching from the soil, thus increasing the N load of those bodies of water affected. Bashkin et al. (1995), for example, estimated that in the years 1987–1991, the Baltic Sea received 8–10% of the N deposited in its catchment area.

Very high  $\text{NH}_3$  concentration in the vicinity of an  $\text{NH}_3$  emission source can damage the plant tissues of coniferous trees (Pitcairn et al. 1998) and of cultivated crops sensitive to  $\text{NH}_3$  (van der Eerden et al. 1998). Animals and humans may experience negative health effects due to large amounts of  $\text{NH}_3$  in the air, which has been observed inside farm animal buildings in particular (Kangas et al. 1987).

$\text{NH}_3$  losses from manure are also harmful from the agronomic point of view, because they decrease the amount of manure N available for the crop. In Finland, the loss of  $\text{NH}_3\text{-N}$  from manure in 2004 corresponds to 15% of the N contained in fertilizers sold to Finnish farms (TIKE 2004). Although some of the volatilized  $\text{NH}_3$  is deposited on agricultural land and taken up by the crop,  $\text{NH}_3$  emissions from manure represent a loss of N from the nutrient cycle of agriculture to the environment. Therefore, controlling  $\text{NH}_3$  emissions is of great concern in manure management both from an environmental and from an agronomical point of view.

### **1.3.5 $\text{NH}_3$ volatilization from manure in the field**

Most of the  $\text{NH}_3$  emissions from manure occur in the field after slurry application (Bussink and Oenema 1998, van der Hoek 1998). Bussink and Oenema (1998), Ni (1999), Sommer and Hutchings (2001) and Sommer et al. (2003) have provided reviews of  $\text{NH}_3$  volatilization and its reduction.

$\text{NH}_3$  volatilization is usually fastest in the first few hours after the application (e.g. Pain et al. 1989, Sommer and Christensen 1990, Svensson 1994a). Volatilization of carbon dioxide from manure increases pH (Sommer et al. 1991, Dendooven et al. 1998, Chantigny et al. 2004a), which enhances the volatilization of  $\text{NH}_3$ . Drying of the manure accelerates  $\text{NH}_3$  volatilization by increasing the concentration of ammoniacal N in the liquid phase of the manure

(Lauer et al. 1976), but may also limit  $\text{NH}_3$  loss through surface crusting (Sommer et al. 1991, Thompson and Meisinger 2002).

Weather conditions affect  $\text{NH}_3$  volatilization in many ways. Warm, sunny, dry, and windy weather favours volatilization (Braschkat et al. 1997, Sommer and Olesen 2000, Gordon et al. 2001, Huijsmans et al. 2003, Misselbrook et al. 2005b). Increasing wind speed, temperature, and solar radiation accelerate the movement of  $\text{NH}_3$  from manure into air, and also enhance the drying of manure unless the relative humidity of the air is high. Rising temperature also promotes the volatilization of  $\text{NH}_3$  by accelerating the diffusion of  $\text{NH}_3$  in the manure to manure surface, and by increasing the partial pressure of  $\text{NH}_3$  in the liquid phase of manure. Because of diurnal variation in weather conditions,  $\text{NH}_3$  volatilization is usually highest in the daytime (Beauchamp et al. 1982, Bussink et al. 1996, Neftel et al. 1998), and application of manure in the evening frequently results in lower  $\text{NH}_3$  losses than does application in the middle of the day (Gordon et al. 2001). Rain or irrigation can reduce  $\text{NH}_3$  volatilization (Sommer and Christensen 1990, Misselbrook et al. 2005b) by washing manure and ammoniacal N into the soil. The risk for  $\text{NH}_3$  losses is higher when manure is spread in the summer than it is in cooler seasons because of warmer weather and longer days of summer, especially in northern latitudes.

$\text{NH}_3$  volatilization from surface-applied slurries can be high meaning virtually total loss of ammoniacal N (e.g. Braschkat et al. 1997, Huijsmans et al. 2003). Rapid infiltration of slurry into the soil, however, reduces  $\text{NH}_3$  emissions. Recently tilled soil, in particular, may have a high capacity to absorb slurry, which keeps  $\text{NH}_3$  volatilization low (Sipilä 1992, Sommer and Ersbøll 1994, de Jonge et al. 2004). In grassland, the soil surface is often more compacted than in arable land, and grass sward prevents slurry from reaching the soil, which reduces infiltration and increases  $\text{NH}_3$  loss (Stevens and Logan 1987, Thompson et al. 1990, Döhler 1991). Clay content has proven to be an important factor controlling  $\text{NH}_3$  volatilization from surface-applied slurry in Finnish soils (Kemppainen 1989, p. 258). Clay binds  $\text{NH}_4^+$  through both cation exchange and dissolution in water within clay aggregates. Kemppainen (1989, p. 258) observed that soil pH was not useful as a general criterion for  $\text{NH}_3$  volatilization assessment, but a single rise in soil pH increases  $\text{NH}_3$  volatilization.

The type of manure affects  $\text{NH}_3$  volatilization, because manures differ in their content of ammoniacal N, pH, and physical properties (Table 1). When applied to the surface, cattle slurry often loses a larger portion of its ammoniacal N than does pig slurry because with a higher content of dry matter, cattle slurry infiltrates less into the soil (Döhler 1991). Also, the different composition of dry matter in pig and cattle slurries explains the greater infiltration capacity of pig slurry (Misselbrook et al. 2005c). Surface-applied solid manure remains on the soil, which renders it more prone to high relative

losses than slurry (Lauer et al. 1976, Svensson 1994a, Rodhe and Karlsson 2002, Webb et al. 2004). However, the content of ammoniacal N is often lower in solid manure than in slurry (Kempainen 1989).

NH<sub>3</sub> volatilization can be reduced by the appropriate treatment and application of manure. Aeration and mechanical separation of solid matter reduce the dry matter content and viscosity of manure slurry, and thereby decrease the smothering of crops by the slurry, and enhance the infiltration of slurry into the soil. This may reduce NH<sub>3</sub> volatilization (Frost et al. 1990, Braschkat et al. 1997). However, aeration increases the temperature and pH of slurry, which can promote the volatilization of NH<sub>3</sub> (Pain et al. 1990, Leinonen et al. 1998). Therefore, NH<sub>3</sub> emissions may not be significantly reduced (Morken 1992), or may even increase (Amon et al. 2006). Separation may be more efficient in reducing the dry matter content of slurry, and researchers have observed considerable reductions in NH<sub>3</sub> volatilization (Morken 1992, Amon et al. 2006). If, however, lower DM content fails to enhance the infiltration of slurry, it may even accelerate NH<sub>3</sub> emission, because slurry droplets are smaller, and therefore applied slurry has a larger surface area (Braschkat et al. 1997).

Incorporation of surface-applied slurry can reduce NH<sub>3</sub> volatilization if manure is well covered by the soil (Sommer and Christensen 1990, Sipilä 1992, Svensson 1994a, Thompson and Meisinger 2002, Wulf et al. 2002). If weather conditions promote volatilization, the work must be carried out within a few hours to achieve a significant reduction in NH<sub>3</sub> emission (Wulf et al. 2002). For example, Huijsmans and de Mol (1999) concluded that because of longer time-lag between application and incorporation, incorporation by ploughing resulted in a greater NH<sub>3</sub> emissions than did incorporation by a cultivator, even though ploughing incorporates manure more thoroughly. The injection of slurry into the soil reduces NH<sub>3</sub> volatilization (Frost 1994, Dosch and Gutser 1996, Misselbrook et al. 1996), because slurry flows into the soil directly from the spreader. The effectiveness of injection and incorporation in the reduction of NH<sub>3</sub> losses varies depending on prevailing conditions (Smith et al. 2000). When slurry is applied at a moderate rate to soil with a high capacity to absorb slurry, differences between surface application and incorporation or injection may be small (Vandré and Kaupenjohann 1998, Misselbrook et al. 2002). Injectors may function differently in different soils. For example, most of the injectors used by Rodhe and Rammer (2002) and Rodhe and Etana (2005) functioned unsatisfactorily in soils with high clay content, but Misselbrook et al. (2002) observed no effect by soil type even though they, too, injected slurry into clay soils. As a consequence of reduced NH<sub>3</sub> losses, injection increases the content of plant-available N in soil, which may result in NH<sub>3</sub> volatilization from plants (Mattson et al., 1998). A higher content of N in the soil can also enhance N losses through the emission of dinitrogen and N oxides (e.g. nitrous oxide) from nitrification and denitrification, but the effect may vary widely between different envi-



ronmental and soil conditions (Clemens et al., 1997, Rubæk et al., 1996, Thompson et al., 1987).

Band spreading may reduce  $\text{NH}_3$  volatilization (Frost 1994, Reitz et al. 1999, Sommer and Olesen 2000), because the surface area of band-spread slurry is smaller than that of broadcast slurry, and when applied to a growing crop, air flow on slurry is reduced. Svensson (1994a) observed that initially  $\text{NH}_3$  volatilized from band spread slurry at a lower rate than from broadcast slurry, but the total emission differed only slightly. A taller and denser canopy reduces wind speed more, and has a higher potential to absorb  $\text{NH}_3$  (Sommer et al. 1997). However,  $\text{NH}_3$  concentration in the air must exceed the compensation point to enable  $\text{NH}_3$  uptake by the leaves (Farquhar et al. 1980), and the ability of the crop to absorb  $\text{NH}_3$  may be lower in later stages of growth (e.g. at stem elongation) (Sommer et al. 1997). In a study by Mannheim et al. (1995),  $\text{NH}_3$  emissions on arable land were greatest under a 10-cm high canopy, where plants prevented part of the applied manure from reaching the soil, but did not significantly reduce wind speed or solar radiation on the soil surface.

## **1.4 Utilization of manure N in crop production**

Almost all manure is used for the fertilization of agricultural crops. The fertilizer effect of manure N is, however, difficult to predict. In addition to ammoniacal N, which is a readily plant-available form of N, manure contains organic matter which may release ammoniacal N through mineralization, but on the other hand, may reduce the amount of plant-available N through immobilization. Also, the susceptibility of ammoniacal N to losses through  $\text{NH}_3$  volatilization makes the N fertilizer effect of manure uncertain. The timing and technique of manure application are not always optimal for the utilization of manure N. For example, application in autumn may lead to losses through leaching, and surface application may cause  $\text{NH}_3$  volatilization.

### **1.4.1 Reactions of manure N in the soil**

The soil can adsorb the ammoniacal N of manure in a plant-available form to cation exchange sites or fix it to the interlayer space of expandable clay minerals. Organic matter and the high pH of manure may enhance the sorption of  $\text{NH}_4^+$  (Fernando et al. 2005). The possible remnants of urea are hydrolysed to  $\text{NH}_4^+$  by the urease enzyme in the soil (Zantua and Bremner 1976). In aerobic conditions, a large part of  $\text{NH}_4^+$  is nitrified into  $\text{NO}_3^-$  (Paul and Beauchamp 1994, Griffin et al. 2002) or immobilized into soil microbial biomass within a few weeks (Jensen et al. 2000, Sørensen 2004), unless low temperature or lack of moisture prevent microbial activity. Nitrification may produce some gaseous N losses (Paul et al. 1993). The immobilized N enters the mineralization-immobilization turnover of N in the soil, from which it may be released in a plant-available form (Paul and Beauchamp 1994 and 1995) but it may

also remain in the soil organic matter which is recalcitrant to decomposition (Sørensen 2004). The readily-decomposable organic matter of manure enhances the microbial activity of soil (Calderón et al. 2004) and may increase N immobilization (Kirchmann and Lundvall 1993), but an increase in the gross rate of N transformations does not necessarily affect the net rate of N mineralization or immobilization (Luxhøi et al. 2004). Immobilization may be considerable particularly if manure contains straw or other organic material with a high C/N ratio (Meyer and Sticher 1983, Sørensen 1998). Microbial immobilization and fixation into clay minerals reduce the amount of plant-available ammoniacal N in the soil (Trehan and Wild 1993, Paul and Beauchamp 1994, Chantigny et al. 2004b), but the mineralization of readily decomposable organic matter of manure may partially compensate for this (Kirchmann 1985, p. 51, Luxhøi et al. 2004, Sørensen 2004). A substantial part of both immobilized and fixed N may be released during the same growing period, but the availability of N is delayed. In some cases manure produced no significant increase in N mineralization after the immobilization phase (e.g. Flowers and Arnold 1983, Kirchmann 1991).

The fixation of  $\text{NH}_4^+$  into clay minerals is approximately as strong as that of potassium (Dissing Nielsen 1972). A high concentration of potassium can reduce the fixation of  $\text{NH}_4^+$  (Dou and Steffens 1995), and thus the adsorption of  $\text{NH}_4^+$  in potassium-rich cattle manure may be less than in other manures. Microbial activity may promote the release of recently fixed  $\text{NH}_4^+$ , especially with a lot of organic matter available as an energy source to the microbes (Breitenbeck and Paramasivam 1995).

Heavy rains may cause losses of manure N through leaching (Kemppainen 1995, Leclerc et al. 1995) and, if soil conditions turn anaerobic, through denitrification. The risk of denitrification of soil  $\text{NO}_3^-$  exists also immediately after the application of slurry (Paul et al. 1993, Calderón et al. 2004), because soil becomes wet and slurry contains a lot of organic compounds which denitrifying bacteria can use as energy sources (Paul and Beauchamp 1989).

### **1.4.2 Crop uptake of manure N**

The short-term fertilizer effect of manure strongly depends on its content of inorganic N (Beauchamp 1987, Hansen 1996, Zebarth et al. 1996, Petersen 2003, Sørensen et al. 2003, Sieling 2004, Salazar et al. 2005), which usually consists mainly of ammoniacal N. It is readily plant-available, but its immobilization, which is enhanced by the organic matter of manure, reduces and retards the N fertilizer effect of manure. This is significant, especially in the fertilization of spring cereals in areas with a short growing season, such as Finland, because in these conditions, N uptake is concentrated into a relatively short period in spring and early summer. The degree of N release from the organic matter of manure is in most cases low and differs little from the release of N from soil

organic matter (Beauchamp 1987, Kirchmann 1991, Honeycutt et al. 2005). C/N and N content seem to correlate with the release of N from organic matter in manure (Kirchmann 1985, p. 60, Stockdale and Rees 1995, Sørensen et al. 2003, Calderón et al. 2004, Griffin et al. 2005, Gutser et al. 2005), but its contribution to plant-available N is uncertain and difficult to predict. Rees and Castle (2002) observed a positive correlation between the content of water-soluble organic carbon in the manure and total N uptake by spring barley at harvest. Furthermore, soil properties, such as the content of clay and organic matter, affect the dynamics of manure N (e.g. Sørensen and Amato 2002, Luxhøi et al. 2004, Honeycutt et al. 2005). Similarly to organic matter in soil, organic matter in manure releases N more in later stages of the growing period, which makes this N more beneficial for forage and root crops than for cereals. For example, Hansen (1996) observed that cattle manure applications had no residual effect on the yield of oats, whereas tended to produce higher yields in ley that uses the released N more effectively in the later part of growing season.

The supplementation of manure with inorganic fertilizer N can compensate for the initially low availability of manure N and balance the amounts of applied nutrients. The ratio of P and K to N in manure is often higher than what crops demand, and losses of manure N, for example through  $\text{NH}_3$  volatilization, exacerbate the deficiency of N. The combination of manure and inorganic fertilizer has proven recommendable to achieve high crop yield, but the apparent recovery of applied N is not always increased (Kemppainen 1989, p. 212–213, Petersen 1996, Beckwith et al. 2002).

In most cases, surface-applied slurry has a weaker N fertilization effect than does slurry incorporated into the soil (Kemppainen 1989, p. 202–219, Petersen 1996, Smith et al. 2000, Sørensen and Amato 2002, Sørensen 2004, Sørensen and Thomsen 2005, Coelho et al. 2006).  $\text{NH}_3$  volatilization reduces the recovery of ammoniacal N from surface-applied slurry. Another possible factor, especially in dry conditions, is the adsorption of ammoniacal slurry N to the very top of the soil, where it is unavailable to the roots. In Kemppainen's (1989) experiments, injection in some cases produced a higher recovery of dairy cow slurry N in spring barley yield than did surface application, but when the application was followed by wet conditions, injection resulted in even lower recovery. With high precipitation, the difference between the application technique was small. Smith et al. (2000) found that band spreading, and especially injection of dairy slurry, for winter wheat in spring tended to increase cereal grain yield and N uptake relative to broadcast spreading. Mooleki et al. (2002) observed a clear increase in the utilization of pig slurry N by spring cereals and canola when injection was compared to surface spreading and consequent incorporation in autumn or spring application.

## 1.5 Use of peat in manure treatment

$\text{NH}_3$  volatilization from manure can be reduced by adding materials that bind  $\text{NH}_4^+$  or lower pH or both. Peat adsorbs ammoniacal N effectively and can prevent  $\text{NH}_3$  losses (Virri 1941, Kemppainen 1987a, Witter and Kirchmann 1989b, Al-Kanani et al. 1992, Jeppson 1999, Siva et al. 1999, Rizzuti et al. 2002). Therefore, it has served as a bedding material for domestic animals in Finland and in other areas where it is available. Peat can also have a positive effect on moisture conditions in the soil (Pietola and Tanni 2003). In the long run, peat and manure applications will increase soil organic matter and improve soil structure (Persson and Kirchmann 1994, Gerzabek et al. 1995). The most suitable type of peat for manure treatment is moderately humified Sphagnum peat. Its high cation exchange capacity (Puustjärvi 1956) enables it to adsorb  $\text{NH}_4^+$  in a plant-available form, and it also has a high capacity to absorb water (Puustjärvi 1976).

A new way to use peat is to mix it with manure slurry using a machine designed for this purpose (Paper IV). The impregnation of slurry into peat converts the slurry into solid peat manure, which can be stored in heaps. The method is especially useful on farms where slurry storage capacity is insufficient for the whole amount of slurry accumulated during winter. The Finnish application of the European Union's  $\text{NO}_3^-$  directive disallows the spreading of manure in the field between 15 October and 15 April (VNa 931/2000). Mixing the surplus slurry with peat reduces the need to spread slurry in autumn. Postponing manure application until spring usually reduces leaching losses of manure N (Kemppainen 1995, Turtola and Kemppainen 1998) and improves its utilization by crops (Kemppainen 1989).

Manure spreading and incorporation into the soil before sowing in the spring is often a problem because of wet soil and the shortage of time. Although there is more time for manure application and the soil is usually drier after sowing, manure must then be broadcast on the soil surface, and manure N is less available to plants and is susceptible to losses through  $\text{NH}_3$  volatilization. Peat can reduce volatilization by adsorbing  $\text{NH}_4^+$ .

Peat decomposes slowly (Persson and Kirchmann 1994) and the ammoniacal N of peat manure is not immobilized to as large an extent as, for example, the ammoniacal N of straw manure. In a pot experiment where manures and fertilizers were mixed into the soil in a similar way, Kemppainen (1987b) observed that the ammoniacal N of peat manure made with dairy cattle slurry was as effective as the N of inorganic fertilizer. In the experiments of Gagnon et al. (1998), straw manure failed to contribute to soil inorganic N, whereas peat manure increased soil N early in the growing season. The increase occurred mainly with the inorganic N of peat manure, whereas the organic fraction showed a negligible effect. These results confirm that the organic matter of peat is recalcitrant to microbial decomposition.

## 1.6 Objectives of the study

Various alternatives are available in manure management. The experiments presented in this work were carried out to compare different methods of manure treatment and application in relation to their effect on  $\text{NH}_3$  emissions in the field and on N uptake by the crop. In the experiment with peat addition to manure, the effect of peat on soil properties was also investigated. The aim was to find ways to improve the utilization of manure N and to reduce its release into the environment. Study of N emissions was limited to the volatilization of  $\text{NH}_3$  in the field after manure application. The recovery of N in crop yields describes the overall efficiency of N utilization, and thus indirectly the portion of manure N susceptible to escape into the environment through various ways. The experiments were carried out under the conditions of Finland's short growing season, which permits fewer manure applications and requires higher application rates than do areas with a longer growing season.

The following was sought to investigate:

### *a) Application technique and treatment of manure slurry*

Compared to broadcast spreading, can band spreading and injection of manure slurry reduce the volatilization of  $\text{NH}_3$  from slurry applied to fields growing ley or cereals? What is the effect of the application technique on the crop's uptake of manure N? Can the reduction of the dry matter content through aeration or separation reduce  $\text{NH}_3$  emission from slurry and increase N uptake by ley?

### *b) Supplementary N fertilization*

What is the effect of supplementary N fertilization on the crop's overall utilization of manure and fertilizer N?

### *c) Use of peat in manure treatment*

Can the addition of peat to manure slurry limit the volatilization of  $\text{NH}_3$  from manure applied to the field and enhance the crop's utilization of manure N? Can peat also enhance crop growth through its effect on soil structure and moisture conditions?

## 2 Material and methods

### 2.1 Experiments

This work presents results from three Finnish research projects, in which the volatilization of  $\text{NH}_3$  from field-applied manure and the crop's utilization of

manure N were investigated. Papers I and II deal with field experiments in which aerated, separated, or untreated cattle slurry was applied to ley after the first cut in summer by broadcast spreading, band spreading, or injection. The experiments were carried out on clay loam in Jokioinen and on fine sand and *Carex* peat in Ruukki. In the experiments of paper III, which were on clay loam and gyttja clay in Vihti, pig slurry was applied to spring wheat before sowing or in the early stages of growth by broadcast spreading, band spreading, or injection. In papers IV and V, pig slurry as such, or mixed with peat, was applied to spring barley before or after sowing on clay loam in Jokioinen. The *Carex* peat was of the grade used as bedding material on Finnish farms. It is extracted from a depth between little-humified surface peat, which is used as a growth substrate in horticulture, and far-humified peat from deeper layers, which is used as fuel. The degree of humification was H3 on the van Post scale. Details of the experiments appear in the individual papers.

## 2.2 Experimental sites

The soils in Jokioinen were tentatively classified as a Vertic, Stagnic Cambisol (Table 4). The locations in Ruukki included a Sapric Histosol with a layer of *Carex* peat (thickness about 70 cm) overlying a subsoil consisting of fine sand (dominated by the fraction of 0.06–0.2 mm), and a Haplic Regosol where texture, up to the soil surface, also consisted of fine sand. Until some 50 years ago, the Sapric Histosol had received mineral soil as an amendment, and in the late 1980s, digging of open drains had brought some fine sand to the Ap horizon. In Vihti, the experiments took place on a Vertic, Stagnic Cambisol and a Haplic Gleysol reclaimed from a drained lake several decades ago. All the soils are artificially drained with subsurface tile lines installed to the depth of 1–1.2 m, which is considered normal practice in Finland. In principle, this suggests that the soils have aquic moisture regimes. However, the fine sand of Ruukki has also natively been better drained than the other experimental soils, which exhibit naturally poor or somewhat poor drainage.

Compared with the native pH, the pH values of the plough layers have been substantially elevated by repeated liming. Liming has probably affected the pH of the upper B horizons as well. On the basis of measurements made in other similar soils (Yli-Halla et al. 2000), the gyttja clay of Vihti and the organic and fine sand soil of Ruukki likely have a low base saturation at least deeper in the subsoil, while the other soils are likely to have a high base saturation throughout the profile.

Table 4. Soil properties of the experimental sites. Soil names and drainage classes defined according to USDA-NRCS (2002) and FAO (2006).

Location	Soil name	Natural drainage class	Crop	Horizon <sup>1)</sup> / Depth, cm	Texture	Org. C, %	pH	P <sup>2)</sup>	K <sup>2)</sup>	Ca <sup>2)</sup>	Mg <sup>2)</sup>	Paper
										mg l <sup>-1</sup>		
Jokioinen	Vertic, Stagnic Cambisol (Eutric)	Somewhat poorly drained	Ley	Ap	Clay loam	4.4	5.5	12.3	450	1820	450	I, II
				B	Clay loam	3.7	5.9	11.2	330	2130	470	
Ruukki	Sapric Histosol (Dystric, Drainic)	Poorly drained	Ley	Ap	Carex peat	32	5.3	13.2	110	1900	240	I, II
				B	Carex peat		4.7	10.0	63	1350	190	
	Haplic Regosol (Dystric, Oxyaquic, Arenic)	Well drained	Ley	Ap	Fine sand	2.9	5.8	23.7	120	670	89	I, II
				B	Fine sand		6.4	18.6	97	670	95	
Vihti	Haplic Gleysol (Humic, Dystric, Clayic, Drainic)	Poorly drained	Spring wheat	0–20	Gyttja clay	5.0	6.6	2.5	70	2570	212	III
	Vertic, Stagnic Cambisol (Eutric)	Somewhat poorly drained	Spring wheat	0–20	Clay loam	2.2	6.0	15.8	270	2350	318	III
				20–40	Clay	1.1						
Jokioinen	Vertic, Stagnic Cambisol (Eutric)	Somewhat poorly drained	Spring barley	Ap	Clay loam	3.1	6.7	53.0	236	2920	371	IV, V
				B	Clay loam	1.6	6.9	16.1	208	3090	720	

<sup>1)</sup> The lower limit of the Ap horizon was at a depth of 20–25 cm. The B horizon was sampled down to a depth of 40 cm. The Ap horizon was sampled at a different time and at different locations in the fields than the B horizon.

<sup>2)</sup> Extracted with acid ammonium acetate (0.5 M CH<sub>3</sub>COONH<sub>4</sub>, 0.5 M CH<sub>3</sub>COOH, pH 4.65). Soil:extractant = 1:10 v/v.

<sup>3)</sup> No data.

### 2.3 Methods of analyses and measurements

In the field experiments, a split-plot arrangement was used, and analysis of variance was carried out accordingly. Repeated measures analysis of variance was used in the experiments reported in the summary (sections 2.6 and 3.3) and in paper V. Tukey's test and contrasts (summary and paper V) were used for pairwise comparisons. Effects at an error rate below 5% were considered significant. Variation in the results was expressed with standard error of mean.

The methods used in field and laboratory measurements appear in Table 5. The measurement of  $\text{NH}_3$  volatilization is presented in detail in section 2.4. Measurements of the effect of peat manure on soil moisture, organic carbon, and aggregates are reported in detail in section 2.6 because they are not included in the papers.

Table 5. Methods used in the analyses and measurements of the experiments.

Property	Method	Paper
<i>Crop</i>		
Dry matter	Oven drying (105°C)	II, IV
N of crop stand and yield	Kjeldahl method	II, III, V
	Near infrared reflectance	IV
K, Ca, Mg, P, Na	Dry combustion (450–500°C), extraction (4M HCl), determination by AAS (K, Ca, Mg, Na) and ammonium vanadate method (P)	II
<i>Soil</i>		
NO <sub>3</sub> <sup>-</sup> and NH <sub>4</sub> <sup>+</sup>	Extraction (2M KCl), spectrophotometric determination	II, V
Organic C	Dry combustion	Summary
Aggregates: size distribution	Dry sieving	Summary
stability	Wet sieving	Summary
Moisture content	Gypsum blocks	Summary
<i>Manures and peat</i>		
Dry matter	Oven drying (105°C)	I, III, IV, V
pH	Glass electrode pH meter	I, III, IV, V
Ammoniacal N and NO <sub>3</sub> <sup>-</sup>	Extraction (2M HCl + 2.5M CaCl <sub>2</sub> ), determination of NH <sub>4</sub> <sup>+</sup> by distillation, (repeated distillation with Devarda alloy for NO <sub>3</sub> <sup>-</sup> , paper V only)	I, III, IV, V
Total N	Kjeldahl method	I, III, IV
K, Ca, Mg, P	Dry combustion (450–500°C), extraction (4M HCl), determination by AAS (K, Ca, Mg) and ammonium vanadate method (P)	I
Volatilization of NH <sub>3</sub>	Equilibrium concentration technique (JTI method)	I, III, V
<i>Weather conditions during NH<sub>3</sub> measurements</i>		
Temperature	Thermohygrograph	I, III
	Psychrometer	V
Relative humidity	Thermohygrograph	I, III
	Psychrometer	V
Wind speed	Cup anemometer	I, III, V



## 2.4 Measurement of NH<sub>3</sub> volatilization

The methods used to measure NH<sub>3</sub> emissions from field-applied manure can be divided into micrometeorological methods, which usually require a large uniform area (about 1 ha or more), and into chamber or wind tunnel methods, which can be used on small plots but fail to measure NH<sub>3</sub> emission in actual ambient conditions. A review of the techniques for measuring NH<sub>3</sub> volatilization in the field is provided by McGinn and Janzen (1998).

The equilibrium concentration technique (JTI method), which was used in the experiments reported here, is an approach that combines the measurement of NH<sub>3</sub> volatilization in ambient conditions with the use of small plots. The method is described in detail by Ferm and Svensson (1992) and Svensson (1994b), and was evaluated by Misselbrook and Hansen (2001) and Misselbrook et al. (2005d). It was developed in the Swedish Institute of Agricultural Engineering and has been used in several experiments (e.g. Svensson 1994a, Weslien et al. 1998, Ferm et al. 1999, Rodhe and Karlsson 2002, Rodhe and Rammer 2002).

The calculation of volatilized NH<sub>3</sub> is based on the assumption that diffusion of NH<sub>3</sub> through an air layer a few millimetres thick on the surface of soil or applied manure is the main factor limiting the movement of NH<sub>3</sub> into the air (Figure 2). In this layer, air flow is laminar and NH<sub>3</sub> is transported vertically by diffusion only. Turbulence in the air above the layer moves NH<sub>3</sub> much faster than does diffusion.

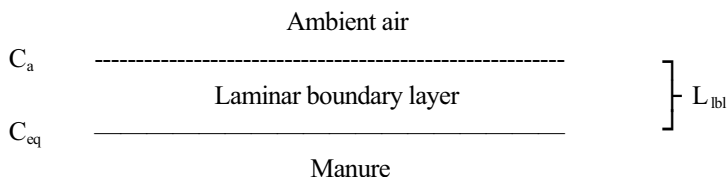


Figure 2. The laminar boundary layer (LBL) in the air above a manure surface.  $C_a$  = ammonia concentration above LBL,  $C_{eq}$  = ammonia concentration at the interface of LBL and manure,  $L_{lbl}$  = thickness of LBL.

Diffusion of NH<sub>3</sub> through the laminar boundary layer (LBL) occurs according to Fick's law, and is described by the equation

$$E = (C_{eq} - C_a)D / L_{lbl} \quad (1)$$

where  $E$  is the amount of emitted NH<sub>3</sub> per area and time,  $C_{eq}$  is the equilibrium concentration of NH<sub>3</sub> in the air at the very surface of soil or manure, which is also the lower edge of the LBL,  $C_a$  is the concentration of NH<sub>3</sub> in the air above the LBL,  $D$  is the diffusion coefficient for NH<sub>3</sub> in the air, and  $L_{lbl}$  is

the thickness of the LBL, which depends on wind speed and smoothness of the surface.  $D$  depends on temperature ( $T$ ) and is calculated by the equation

$$D = T^{1.5} \times 4.59 \times 10^{-9}. \quad (2)$$

The effect of  $D$  and LBL on  $\text{NH}_3$  volatilization can be denoted as a mass transfer coefficient ( $K$ ), which is a meteorological parameter that describes how fast a substance can move through a layer of air:

$$K = D/L_{\text{LBL}} \quad (3)$$

$C_a$  represents the ability of ambient air to receive volatilized  $\text{NH}_3$ ,  $C_{eq}$  indicates the potential of manure to emit  $\text{NH}_3$ , and  $K$  represents the barrier which LBL sets for the flux of  $\text{NH}_3$  from manure to ambient air, which essentially depends on wind speed and temperature. High  $C_{eq}$ , low  $C_a$ , and high  $K$  result in large emissions of  $\text{NH}_3$ .

Air temperature at the soil surface must be measured for the calculation of  $D$ . The emission of  $\text{NH}_3$  during a measurement period is obtained by multiplying  $E$  with the duration of the period.

To obtain an estimate of total emission,  $\text{NH}_3$  volatilization between measurement periods is interpolated with a procedure described by Malgeryd (1996), which takes into account the actual temperature and wind speed prevailing during the intervals. Total emissions are calculated by adding up the emissions of measurement periods and their intervals. The average emission of  $\text{NH}_3$  during an interval of two consecutive measurement periods ( $E_i$ ) is calculated with the equation

$$E_i = C_{f_C} \times C_{f_K} \times (E_n + E_{n+1})/2 \quad (4)$$

where  $C_{f_C}$  is the correction factor for the effect of temperature on the concentration of  $\text{NH}_3$  in the air,  $C_{f_K}$  is the correction factor for the effect of temperature and wind speed on  $K$ , and  $E_n$  and  $E_{n+1}$  are the measured emissions of  $\text{NH}_3$  during the periods before and after the interval, respectively. The calculation of  $C_{f_C}$  and  $C_{f_K}$  is presented by Malgeryd (1996). Correction based on temperature and wind speed renders the estimated emissions more accurate, but variations in solar radiation and air humidity, for example, may affect  $\text{NH}_3$  volatilization in a manner not explained by variations in temperature. The risk for significant discrepancies between estimated and actual emissions increases with the increasing length of the interval and with increasing differences in weather conditions between the interval and the measurement periods.

The JTI method uses passive diffusional  $\text{NH}_3$  samplers placed at the soil surface (Figures 3 and 4). The samplers contain a filter paper impregnated with

oxalic acid, which absorbs  $\text{NH}_3$  from the air by forming  $\text{NH}_4^+$  oxalate. There are two types of sampler which differ in the position of the absorbing filter paper. In the L-type sampler, the paper is mounted at the top of the sampler and is in direct contact with the ambient air. In the C-type sampler, the paper is at the bottom of the sampler, and at the top is a membrane filter, which allows the diffusion of  $\text{NH}_3$  into the sampler but prevents any turbulence inside the samplers. Thus, an L sampler absorbs more  $\text{NH}_3$  than a C sampler does, because with the L sampler,  $\text{NH}_3$  must diffuse only through the LBL above the sampler, but with the C sampler the diffusion path includes the distance from the top to the bottom of the sampler as well. The calculation of  $L_{\text{Lbl}}$  is based on the difference in the amount of  $\text{NH}_3$  absorbed by the two types of the samplers exposed together.

Exposing L and C samplers in ambient air enables the calculation of  $C_a$  and  $L_{\text{Lbl}}$ . For the determination of  $C_{\text{eq}}$ , a ventilated chamber is used.  $C_{\text{eq}}$  could be determined directly as the  $\text{NH}_3$  concentration of a closed chamber placed over the source of  $\text{NH}_3$  emission, but in many cases water would condense on the inner walls of the chamber, disturbing the measurement through absorption of  $\text{NH}_3$  from the chamber air. The development of the JTI method included the construction of a ventilated chamber where the concentration of  $\text{NH}_3$  ( $C_{\text{ch}}$ ) was as close to  $C_{\text{eq}}$  as possible without the risk of water condensation. The result was a chamber ventilated by a fan at a constant rate, where air flow : covered area =  $4.5 \text{ mm s}^{-1}$ . In very moist conditions, where the relative humidity of air is close to 100%, condensation may occur despite the ventilation. Such conditions may prevail at night or during a heavy rain.

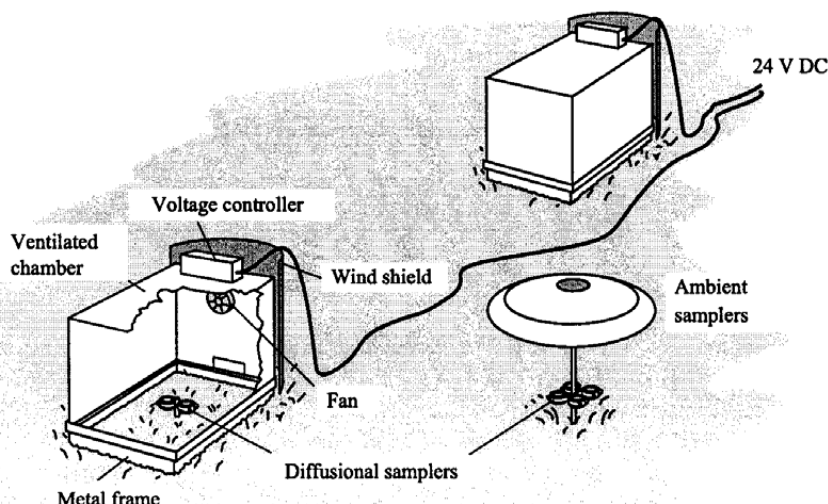


Figure 3. The equipment used for measuring  $\text{NH}_3$  volatilization by the JTI method (Rodhe and Karlsson 2002).

In addition to  $C_{ch}$ , the values of  $C_a$  are also used in the calculation of  $C_{eq}$ , and the air flowing into the chamber is assumed to have the same concentration of  $NH_3$  as that measured with the samplers exposed in the ambient air. Thus, the ambient wind conditions and random variation of the results from samplers exposed in the ambient air to some extent affect the value of  $C_{eq}$ . Values of  $C_{ch}$ , which are calculated only from the results of samplers exposed in the chambers, therefore served as a more stable measure for  $NH_3$  volatilization potential. However,  $C_{eq}$  provides a more general measure of volatilization potential, because it takes into account the effect of the  $NH_3$  concentration in the air flowing into the chambers.

The chambers used in the JTI method have constant ventilation and, therefore, the thickness of LBL under the chambers ( $L_{lbl,ch}$ ) is also constant for a certain type of soil surface. When developing the JTI method, Svensson (1994b) determined a standard value of  $16 \text{ mm s}^{-1}$  for the mass transfer coefficient under chambers ( $K_{ch}$ ) at  $20^\circ\text{C}$  on relatively smooth bare soil. This corresponds to an  $L_{lbl,ch}$  of 1.439 mm. When the method is used on soil with a rough surface or with vegetation,  $L_{lbl,ch}$  may differ from the standard value and should be measured by exposing both C and L samplers in the chambers. Therefore, L samplers were exposed in some of the chambers. With high  $NH_3$  emissions, however, L samplers in chambers are easily supersaturated. To estimate actual  $L_{lbl,ch}$ , results were selected where L samplers in chambers absorbed at least a moderate amount of  $NH_3$ , but were not supersaturated. The range of absorbed  $NH_3\text{-N}$  per sampler was 8–100  $\mu\text{g}$ .

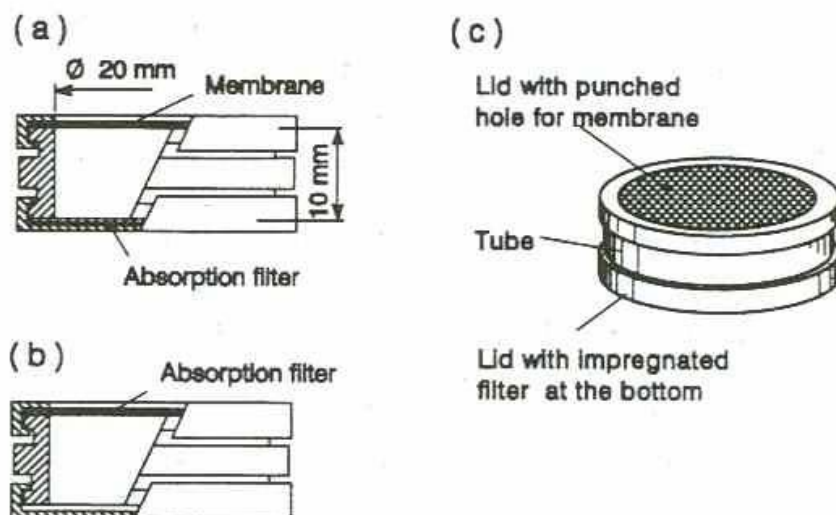


Figure 4. Cross-sections of passive diffusion samplers of types C (a) and L (b), and type C sampler viewed from above (c) (Svensson 1994b).

## 2.5 Recovery of manure N in crop yield

The utilization of applied N was determined with the difference method, where the difference in harvested N between fertilized and unfertilized yields is related to the amount of applied N. The apparent recovery of applied N was calculated with the equation

$$\text{Apparent recovery of N} = \frac{NY_f - NY_0}{NA} \times 100\% \quad (5)$$

where  $NY_f$  = N yield of fertilized crop,  $NY_0$  = N yield of unfertilized crop, and NA = N applied in fertilizer.

The difference method assumes that the supply of N from sources other than fertilizer (e.g. mineralization from soil organic matter and from atmospheric deposition) is equal in fertilized and unfertilized plots. Thus the difference between the plots should result from the fertilization.

Schröder (2005) criticized the difference method for underestimating the N fertilizer value of manures, especially when the application rate of manure exceeds crop demand and the crop used has a low ability to take up N. In the experiments reported here, manure was not applied in excessive amounts and the main aim was to compare the utilization of applied N in different experimental treatments instead of obtaining precise values of the fertilizer value of manure N. Therefore, the difference method is considered applicable in this study. Muñoz et al. (2004) compared the difference method with fertilizer equivalence and  $^{15}\text{N}$  recovery methods in determining the recovery of manure N. They found no significant difference between the methods, but noted that the conditions of control plots greatly influenced the N recovery values obtained. However, when the control treatment is the same for the compared treatments, the differences between the treatments remain unaffected.

## 2.6 Effect of peat manure on soil moisture, organic carbon, and aggregates

The effect of peat manure on soil moisture conditions, soil organic carbon concentration and the stability of soil aggregates was investigated in the experiment reported in papers IV and V. The results reported here do not appear in those papers.

In the autumn preceding the start of the experiment, the whole field was ploughed, but in each autumn thereafter, two of the four replications were ploughed to a depth of 20–22 cm with a mouldboard plough and the other two were stubble mulch tilled to a depth of 13–15 cm with a field cultivator. In 1994, when studying the residual effect of the treatments applied in previ-

ous years, the two different primary tillage methods were considered an experimental treatment. The introduction of a new treatment reduced the number of replications to two. All the plots received 40 kg ha<sup>-1</sup> N as an inorganic NPK fertilizer (20-4-8) placed into the soil at sowing of spring barley with a combine drill. Manures were not applied and none of the plots were irrigated.

### **2.6.1 Soil analyses**

The moisture content of the soil was measured in the years 1990–1993, when the experimental treatments were applied to the plots, with gypsum blocks placed at a depth of 15 cm. Soil samples were taken in early July 1994, before ear emergence in plots that were either unirrigated or irrigated twice in previous years. In the inorganic fertilizer treatment, N levels 0 and 80 kg ha<sup>-1</sup> were sampled. Each soil sample was taken with a special bucket from a depth of 0–10 cm and from a 10 cm x 100 cm area where the barley stand was cut away.

A portion of each soil sample was dried at room temperature for the determination of organic carbon by dry combustion (Sippola 1982) and for the analysis of soil aggregates. The distribution of the aggregates into diameter fractions <2 mm, 2–6 mm and >6 mm was studied by dry sieving of 230–350 g of each air-dry soil sample. Aggregate stability was determined by wet sieving: 20 g of the soil that remained between the 2-mm and 6-mm mesh sieves in dry sieving was spread on a 2-mm mesh sieve, and the sieve was moved up and down in water 44 times within 1 min. The soil remaining on the sieve was washed onto a filter paper, dried at 105°C overnight, and weighed.

### **2.6.2 Statistical analyses**

The results of soil moisture content were analysed with repeated measures analysis of variance using the MIXED procedure of SAS statistical software version 6.08 (SAS Institute Inc. 1990 and 1992). Pairwise comparisons were carried out using contrasts (Steel and Torrie 1981).

Analysis of variance was performed for the results of soil organic carbon, soil aggregates and grain yield measured in slurry and peat manure plots according to the split-plot design with the GLM procedure of SAS statistical software version 6.12 (SAS Institute Inc. 1990). The stripwise arrangement of some treatments was considered in determining the structure of the error terms (Steel and Torrie 1981). The effects of the application method and supplementary fertilization were analysed separately for slurry and peat manure because the arrangement of these treatments differed in slurry and peat manure plots.

## 3 Results and discussion

### 3.1 NH<sub>3</sub> volatilization

#### 3.1.1 JTI method

The JTI method seemed applicable in the experiments reported here.  $L_{\text{lbl}}$  and  $K$  seemed to depend on wind speed and, to a lesser extent, on the properties of the soil surface (Table 6). The largest values of  $L_{\text{lbl}}$  and, correspondingly, the lowest values of  $K$  were obtained from periods with low wind speed. With the emission of NH<sub>3</sub>, the difference between  $C_{\text{ch}}$  or  $C_{\text{eq}}$  and  $C_{\text{a}}$  should increase with wind speed, because at a higher wind speed, the movement of NH<sub>3</sub> away from the emitting surface with mass flow is faster. This was the case with surface-applied slurries in most of the experiments.

Under the constant air flow conditions of the chambers, plant cover seemed to have some observable effect on LBL. The values of  $L_{\text{lbl,ch}}$  on tilled bare soil were close to the standard of 1.439 mm (Table 7), but with vegetation, they were in most cases somewhat higher. Plants limit air flow and, thus,  $L_{\text{lbl,ch}}$  is thicker. The measured values of  $L_{\text{lbl,ch}}$  were, however, not as high as in the measurements by Misselbrook and Hansen (2001), whose  $K_{\text{ch}}$  values correspond to an  $L_{\text{lbl,ch}}$  of about 1.9 mm on bare soil and about 2 mm or more on short grass.

Wind affects NH<sub>3</sub> volatilization by determining  $L_{\text{lbl}}$  and the rate of mass flow above the LBL. The properties of the soil surface affected  $L_{\text{lbl}}$  and  $K$  only slightly, which may result from the relatively high wind speed in most of the measurements. Sommer and Christensen (1989) observed that there was no significant difference in NH<sub>3</sub> volatilization between different surfaces when wind speed exceeded 4 m s<sup>-1</sup>. When wind speed increases,  $L_{\text{lbl}}$ , which depends on surface properties, decreases and the relative importance of LBL in limiting NH<sub>3</sub> volatilization diminishes.

In practise, there is no uniform LBL over the applied manure in the field. There is both spatial and temporal variation in wind speed and, hence,  $L_{\text{lbl}}$  varies in different positions over the surface of the manure. However, the average  $L_{\text{lbl}}$  measured over the samplers provides a useful estimate of the effect of wind conditions on the volatilization of NH<sub>3</sub>. When measuring in thick vegetation, wind speed may be somewhat higher over the samplers than in the crop stand, because the sampler holder creates some open space above it. In this case, measured  $L_{\text{lbl}}$  is somewhat smaller than the actual average  $L_{\text{lbl}}$  in vegetation.

Table 6.  $\text{NH}_3$  volatilization rate ( $E_{\text{NH}_3\text{-N}}$ ), chamber concentration ( $C_{\text{ch}}$ ), equilibrium concentration ( $C_{\text{eq}}$ ), and ambient concentration ( $C_a$ ) of  $\text{NH}_3$ , thickness of laminar boundary layer ( $L_{\text{bl}}$ ), mass transfer coefficient (K), temperature (T), and wind speed. Results are from the measurement period of manure application day, when volatilization rate was highest. BR = broadcasting, BA = band spreading, IN = injection, INC = incorporation by harrowing.

Soil texture	Crop	Manure	Application technique	$E_{\text{NH}_3\text{-N}}$ $\text{g ha}^{-1}\text{h}^{-1}$	$C_{\text{ch}}$ $\mu\text{g m}^{-3}$	$C_{\text{eq}}$ $\mu\text{g m}^{-3}$	$C_a$ $\mu\text{g m}^{-3}$	$L_{\text{bl}}$ mm	K $\text{mm s}^{-1}$	T $^{\circ}\text{C}$	Wind $\text{m s}^{-1}$	Paper
Clay loam	Recently cut ley	Cattle slurry	BR	4 720	13 080	15 990	2 710	1.9	12.0	16.8	3.5	I
			BA	3 860	8 060	9 960	1 300	1.5	15.0	21.0	6.8	
Carex peat			IN	130	500	580	190	1.4	11.1	17.5	4.6	
Fine sand		Cattle slurry, aerated	BR	6 420	20 500	25 600	2 360	2.5	9.3	19.6	3.6	
Clay loam		Cattle slurry, separated	BR	5 680	12 610	15 660	1 770	1.6	13.8	17.7	4.2	
Gyttja clay	Tilled bare soil	Pig slurry	BR + INC	21	140	150	105	1.6	14.7	18.1	4.5	III
			BA + INC	39	210	230	135	1.5	15.0	18.0	4.6	
			IN + INC	0.1 <sup>1)</sup>	65 <sup>1)</sup>	65 <sup>1)</sup>	64 <sup>1)</sup>	5.0 <sup>1)</sup>	4.9 <sup>1)</sup>	17.9	4.6	
Clay loam	Tilled bare soil	Pig slurry	BR + INC	88	320	380	130	1.9	12.9	25.1	3.6	
			BA + INC	50	280	300	200	1.5	16.1	23.7	3.9	
			IN + INC	26 <sup>1)</sup>	170 <sup>1)</sup>	180 <sup>1)</sup>	120 <sup>1)</sup>	4.6 <sup>1)</sup>	7.3 <sup>1)</sup>	19.6	2.8	
	Spring wheat, 1–2 leaf stage	Pig slurry	BR	270	1 340	1470	880	1.4	14.5	20.5	4.3	
			BA	260	790	910	370	1.4	16.3	21.1	5.0	
			IN	2 <sup>1)</sup>	79 <sup>1)</sup>	82 <sup>1)</sup>	68 <sup>1)</sup>	4.3 <sup>1)</sup>	7.4 <sup>1)</sup>	20.3	5.8	
	Spring wheat, 3–4 leaf stage	Pig slurry	BR	250	2 480	2690	1 750	2.8	8.5	27.7	1.8	
			BA	100	1 570	1670	1 210	3.3	7.2	24.7	1.1	
			IN	-7 <sup>12)</sup>	150 <sup>12)</sup>	133 <sup>12)</sup>	200 <sup>12)</sup>	7.1 <sup>12)</sup>	3.2 <sup>12)</sup>	21.0	0.8	
Clay loam	Tilled bare soil	Pig slurry	BR	89	220	260	79	1.4	15.9	14.9	4.1	V
		Pig peat manure	BR	120	360	440	100	1.6	14.7	14.9	4.1	

<sup>1)</sup> Value is inaccurate because of low rate of  $\text{NH}_3$  volatilization.

<sup>2)</sup> Drift of  $\text{NH}_3$  from other plots disturbed the measurement.



Table 7. Thickness of laminar boundary layer in chambers ( $L_{\text{lbl, ch}}$ ). Results are from the measurements where L samplers in the chambers absorbed at least a moderate amount of  $\text{NH}_3$ , but were not supersaturated (absorbed  $\text{NH}_3\text{-N}$  8–100  $\mu\text{g}$  per sampler). Standard error of mean (SEM) is expressed in italics.

Soil texture	Crop	Application technique	Year	Number of chambers	$L_{\text{lbl, ch}}$ , mm	<i>SEM</i>	Paper
Clay loam	Recently cut ley	Broadcast	1995	11	1,55	<i>0,054</i>	I
			1996	23	1,57	<i>0,040</i>	
			1997	22	1,57	<i>0,048</i>	
		Band	1995	6	1,59	<i>0,049</i>	
			1996	12	1,65	<i>0,046</i>	
			1997	12	1,68	<i>0,073</i>	
		Injection	1997	11	1,67	<i>0,080</i>	
Fine sand	Recently cut ley	Broadcast	1995	2	1,52	<i>0,035</i>	
		Inje ction	1995	2	1,66	<i>0,059</i>	
Carex peat		Broadcast	1996	9	1,39	<i>0,045</i>	
		Injection	1996	9	1,44	<i>0,054</i>	
			1997	2	1,55	<i>0,003</i>	
Clay loam	Tilled bare soil	Broadcast	1999	8	1,49	<i>0,082</i>	
Gyttja clay		Broadcast	1999	4	1,49	<i>0,187</i>	
Clay loam	Spring wheat, 1–2 leaf stage	Broadcast	1999	12	1,46	<i>0,047</i>	
			2000	10	1,68	<i>0,076</i>	
Clay loam	Spring wheat, 3–4 leaf stage	Broadcast	1999	10	1,53	<i>0,097</i>	

The JTI method also was useful for measuring  $\text{NH}_3$  volatilization from band spread or injected manure, which was concentrated in certain parts of the measured area. For example, the values of  $L_{\text{lbl, ch}}$  measured with band spread or injected slurry were somewhat higher, but did not differ substantially from those measured from broadcast slurry (Table 7). Volatilized  $\text{NH}_3$  mixes in the air so that the amount of  $\text{NH}_3$  absorbed by the samplers depends little on whether  $\text{NH}_3$  volatilizes from the whole measured area or only from certain parts of it. However, to test the effect of the position of samplers in relation to manure band or injection slot on the amount of  $\text{NH}_3$  absorbed by the sampler could prove interesting. When measuring  $\text{NH}_3$  volatilization from band spread or injected manure, chambers were placed so that the ratio of band or injection slot length to the covered area was the same as for the whole plot. This way, the  $\text{NH}_3$ -emitting surface per area under the chambers corresponded to that of the whole plot.

When the JTI method is used with a growing crop, the uptake of aerial  $\text{NH}_3$  by plants can lower the value of  $\text{NH}_3$  volatilization obtained, because the plants may reduce the  $\text{NH}_3$  concentration under the chambers more than in the ambient air. In some cases with surface-applied slurry, Ferm et al. (1999) observed an even lower  $\text{NH}_3$  concentration under the chambers than outside. In our experiment, however, the canopies were not as high as in the afore-

mentioned measurements, and in broadcast and band-spread plots the  $\text{NH}_3$  concentration under the chambers was always, and in most cases several times, higher than in the ambient air. In injected plots, both the chamber and ambient concentrations were low (Table 6). The higher  $\text{NH}_3$  concentration may, nevertheless, have increased the uptake of  $\text{NH}_3$  by the grass under the chambers, thus reducing the  $\text{NH}_3$  volatilization values.

The chambers of the JTI method are used for the measurement of  $C_{\text{eq}}$ . The measured value of  $C_{\text{eq}}$  in the chambers is needed for the calculation of  $\text{NH}_3$  volatilization in ambient conditions, which implies that the properties of the manure surface are assumed similar under the chambers and in ambient conditions. However, several factors may create some difference between the chambers and uncovered area. First of all, the distribution of manure and the properties of the soil and vegetation over the measured area usually vary, and therefore several chambers should be used to ensure that the spots covered by the chambers well represent the average conditions of the area. Furthermore, the chambers affect the conditions on the manure surface by reducing solar radiation and by keeping air flow rate over the surface constant, which is often lower than that in ambient air. This affects temperature and moisture conditions. For example, moist soil and manure may dry up at a lower rate under the chambers than in ambient conditions, which was observed in some measurements.  $\text{NH}_3$  volatilization may often proceed faster in ambient conditions than under the chambers, which results in a difference in the amount of ammoniacal N remaining in the manure and, consequently, in the subsequent rate of  $\text{NH}_3$  volatilization. The difference in conditions between the area under the chambers and those of the uncovered area may increase with the duration of the measurement. This can be minimized by changing the location of the chambers between measurement periods, which, however, disturbs the comparison of  $\text{NH}_3$  emissions between the periods, if  $\text{NH}_3$  volatilization between the locations differs.

When chambers are placed on an area emitting  $\text{NH}_3$ ,  $C_{\text{ch}}$  initially equals to  $C_{\text{a}}$ , and only with time approaches the level that corresponds to the chamber conditions. The total amount of  $\text{NH}_3$  absorbed by the samplers in the chambers is, therefore, lower than what it was if  $C_{\text{ch}}$  was at the level corresponding to the chamber conditions from the very beginning of a measurement, as is the assumption in the calculation of  $\text{NH}_3$  volatilization. Thus, the calculated value for  $C_{\text{ch}}$  is somewhat lower than the actual  $C_{\text{ch}}$  in steady chamber conditions. Another assumption, which may not always be fully correct, is that the air flowing into the chambers has the same concentration of  $\text{NH}_3$  as that measured by the samplers placed on the ground in ambient air ( $C_{\text{a}}$ ). If, for example, a chamber is located near the edge of an area treated with manure, wind from the edge may dilute the concentration of  $\text{NH}_3$  to a level lower than  $C_{\text{a}}$ . Another factor affecting the  $\text{NH}_3$  concentration of inflowing air is the possible recirculation of out-flowing air back into the chamber. However, the calculated value of  $C_{\text{eq}}$  depends more on  $C_{\text{ch}}$  than on  $C_{\text{a}}$ .

Despite all the above mentioned factors that affect the results, the JTI method seemed useful, at least for the comparison of  $\text{NH}_3$  volatilization from different treatments, because the differences between the treatments seemed reasonable. In the study reported here, the JTI method was not compared with other methods. In the evaluation by Misselbrook and Hansen (2001), results obtained with the JTI method did not differ significantly from those of the integrated horizontal flux method. Misselbrook et al. (2005d), however, preferred wind tunnels to the JTI method for measurements on small plots, because it was difficult to estimate appropriate exposure times for the samplers, and in some C samplers, the teflon membrane was depressed, which reduces the diffusion distance inside the sampler. The emissions measured from small plots may be higher than from a larger area (Génermont and Cellier 1997), because of the edge effect: air with low  $\text{NH}_3$  concentrations flows to the plots from the surrounding area, lowering  $C_a$  and thus increasing the emission. Future development of the JTI method should include investigation of how the position of the sampler relative to band spread or injected manure and how the difference in conditions between the ambient air and the chambers affect the results.

### **3.1.2 Effect of treatments on $\text{NH}_3$ volatilization**

$\text{NH}_3$  emissions from cattle slurry surface-applied on ley were equivalent to about half of the applied ammoniacal N (Table 8, Paper I). Band spreading retarded volatilization, but total emission did not differ significantly from the emission from broadcast slurry. Aerating the slurry failed to reduce  $\text{NH}_3$  volatilization, but rather tended to increase it, probably because of increased pH. Separation reduced the dry matter content of slurry more than did aeration.  $\text{NH}_3$  emissions from the liquid fraction of the mechanically separated slurry seemed slightly smaller than that from the untreated slurry, but the overall difference was insignificant. The injection of slurry into the soil prevented  $\text{NH}_3$  losses almost completely. The injector with a novel design (Kapuinen 1998) was obviously capable of leaving the slurry slots closed, which is important for the restriction of  $\text{NH}_3$  losses (Rodhe et al. 2004).

$\text{NH}_3$  volatilization from pig slurry surface-applied to tilled bare soil or to the spring wheat stand constituted only a few percent of the applied ammoniacal N at its highest concentration (Table 8, Papers III and V). Incorporation, and especially injection, resulted in even lower emissions. Injection reduced  $\text{NH}_3$  volatilization more than did surface application even when the soil was harrowed after application. Band spreading showed no consistent difference from broadcast spreading.

Generally, the  $\text{NH}_3$  volatilization rate from surface-applied slurries was highest during the first measurement period after spreading, and decreased to a low level within the three to six days of measurements. In some cases, vola-

Table 8. Volatilized  $\text{NH}_3\text{-N}$  as a percentage of applied ammoniacal N in the  $\text{NH}_3$  volatilization experiments. BR = broadcast, BA = band spreading, IN = injection, INC = incorporation by harrowing.

Soil texture	Crop	Manure	Application technique	Manure properties		Time	Volatized NH <sub>3</sub> -N, % of manure NH <sub>4</sub> -N	Paper	
				Rate, Mg ha <sup>-1</sup>	NH <sub>4</sub> -N, DM, pH				
Clay loam, fine sand or Carex peat	Recently cut ley	Cattle slurry	BR	45	95	7.1	7.1	3 d	I
			BA	44	91	7.1	7.1	3 d	
	Cattle slurry, aerated	IN	45	95	7.1	7.1	3 d	0.4	
		BR	49	90	6.5	7.2	3 d	59	
		BR	45	93	4.5	7.3	3 d	42	
Gyttja clay	Tilled bare soil	Pig slurry	BR + INC	31	118	6.6	7.0	3 d	III
			BA + INC	31	118	6.6	7.0	3 d	
	Tilled bare soil	IN + INC	31	118	6.6	7.0	3 d	0.01	
		BR + INC	31	118	6.6	7.0	3 d	0.8	
		BA + INC	31	118	6.6	7.0	3 d	0.7	
Clay loam	Spring wheat, 1–2 leaf stage	Pig slurry	IN + INC	31	118	6.6	7.0	3 d	0.4
			BR	23	105	4.7	7.1	6 d	2.4
	Spring wheat, 3–4 leaf stage	BA	23	105	4.7	7.1	6 d	2.5 <sub>2)</sub>	
		IN	23	105	4.7	7.1	6 d	2.9 <sup>3)</sup>	
		BR	31	118	6.6	7.0	3 d	2.1 <sup>3)</sup>	
Clay loam	Tilled bare soil	Pig slurry	BA	31	118	6.6	7.0	3 d	2.1 <sup>3)</sup>
			IN	31	118	6.6	7.0	3 d	2) <sub>2)</sub>
	Pig peat manure	BR + INC	23	95	6.0	1)	4 h	2)	
		BR	23	95	6.0	1)	8 h	0.5 <sub>2)</sub>	
		BR + INC	34	83	22.0	1)	4 h	0.8	
			BR	34	83	22.0	1)	8 h	

<sup>1)</sup> Not measured.

<sup>2)</sup> Volatilization was so low that it could not be measured.

<sup>3)</sup> Result may have been affected by rain and  $\text{NH}_3$ .

tilization increased after the first period because of higher wind speed. The volatilization potential, described by  $C_{ch}$  and  $C_{eq}$ , diminished with time in all cases, except with some injected or incorporated slurries. Wind speed seemed an important environmental factor affecting the volatilization rate of  $NH_3$  in the experiments. The temperature range of any single experiment was limited, which reduced its significance as a factor creating variation in the volatilization of  $NH_3$ .

Both the actual  $NH_3$  emission and potential  $NH_3$  volatilization ( $C_{ch}$  and  $C_{eq}$ ) were much higher from the surface-applied slurries on ley than on tilled bare soil or on the barley field (Tables 6 and 8). The large difference in  $NH_3$  volatilization between ley and tilled soil indicates the great effect the physical properties of the soil surface have on  $NH_3$  emissions. Tilled soil allows greater infiltration of the slurry than does the more compacted and plant-covered soil of a ley. Untilled grassland soils may also develop higher water repellence than that of tilled soils (Hallett et al. 2001), which further hinders infiltration. The significance of infiltration is indicated by the many times higher  $NH_3$  concentration in chambers placed over slurry applied to plastic film than over slurry applied to tilled bare soil (Paper V). Hoff et al. (1981) and Döhler (1991) obtained a similar result, observing that emissions from manure applied to a plastic film were several times higher than those from manure applied to surface. However, Vandr  and Clemens (1997) found only a small difference in a similar comparison in which the partial freezing of the soil limited slurry infiltration. Sommer et al. (2004) observed that the infiltration of slurry explained a large proportion of the variation in  $NH_3$  volatilisation, despite the large spatial variation. Smith et al. (2000) measured higher  $NH_3$  volatilisation from slurry applied to hard and dry grassland soil than from slurry applied to moist grassland or to arable soil. Excessive moisture, however, may increase  $NH_3$  volatilization (Sommer and Christensen 1990) if it prevents infiltration.

The reduced volatilization of  $NH_3$  from tilled soil is partially attributable to the adsorption of manure ammoniacal N by the clay fraction of the soil (Kempainen 1989, p. 258). Experiments with tilled soil were carried out only on clay soils. In a sandy soil, the adsorption of manure N would probably be less important due to its lower cation exchange capacity, but infiltration also reduces  $NH_3$  volatilisation by preventing direct contact between manure and free air.

Cattle slurry was not investigated on tilled soil. Because of the larger content and different physical structure of dry matter (Misselbrook et al. 2005c), cattle slurry will presumably not infiltrate into the tilled soil to such an extent as pig slurry, and the potential relative loss of cattle slurry N through  $NH_3$  volatilization is greater. The position of applied slurry in the soil has been the focus of some recent studies (Rodhe 2003, Sommer et al. 2004, Misselbrook et al. 2005c), and requires further investigation.

Peat manure showed a low  $\text{NH}_3$  emission on the day of application, <1% of applied ammoniacal N, even though it did not infiltrate into the soil. This indicates that peat has a high capacity to bind  $\text{NH}_3$ . However, during several weeks of mostly dry and warm weather surface applied peat manure lost most of its ammoniacal N. The low rate of  $\text{NH}_3$  volatilization from peat manure allows the incorporation of applied manure to be postponed without the risk for large N losses.

### **3.2 Recovery of manure N by the crops**

The various crops exhibited large differences in the uptake of manure N. The uptake of N depended not only on the extent of  $\text{NH}_3$  losses, but also on the location of the applied manure. On ley,  $\text{NH}_3$  volatilization from surface-applied slurries was large, whereas injection effectively prevented the losses (Table 8, Paper I), which is the apparent reason for the higher N recovery from injected slurry (Table 9, Paper II). When slurry was applied to bare soil or to spring wheat stands in early growth stages, injection or incorporation or both reduced  $\text{NH}_3$  emission, but  $\text{NH}_3$  volatilization from surface-applied slurries was also low (Table 8, Papers III and V). However, the increase in the recovery of manure N achieved by injection, and to a lesser extent by incorporation (Table 10, Papers III and IV), was higher than the reduction in  $\text{NH}_3$  losses. This suggests that injection increased the crop uptake of manure N not only by reducing  $\text{NH}_3$  volatilization, but also by bringing manure deeper into the soil, thus making it more available to the plant roots. However, incorporation did not increase the availability of peat manure N in conditions where surface-applied peat manure retarded evaporation after rain or irrigation, thus increasing the soil moisture available to the crop (Paper IV).

When applied to the surface, solid manure remains on the soil surface and slurry may infiltrate only to a depth of a few centimetres (Chantigny et al. 2004a). Movement of manure N is minor, especially in dry weather conditions, which often prevail in Finland in spring and early summer. In the experiment of Sommer et al. (2004), the  $\text{NH}_4^+$  of surface applied-slurry was absorbed by surface soil and did not infiltrate as deep as the chloride ions of the slurry. Similarly to the chloride,  $\text{NO}_3^-$  moves in the soil more easily than does  $\text{NH}_4^+$ . The ammoniacal N of manure can be converted to  $\text{NO}_3^-$  by nitrifying bacteria, but it must be in a location where conditions permit microbial activity. In the very surface soil, the lack of moisture may prevent nitrification. Compared with incorporation, this could be observed as a higher proportion of  $\text{NH}_4\text{-N}$  in the soil where manure was surface-applied (Paper V). Irrigation or rain can, to some extent, leach ammoniacal N from surface-

Table 9. Apparent recovery of applied ammoniacal N of manures applied to ley after the first cut (paper II). BR = broadcasting, BA = band spreading, INJ = injection.

Soil texture	Manure	Application technique	Apparent recovery of N, %	Years
Clay loam	Cattle slurry	BR	24	1995–1996
		BA	24	
		INJ	32	
	Cattle slurry, aerated	BR	25	
		BA	25	
		INJ	37	
	Cattle slurry, separated	BR	30	
		BA	30	
		INJ	34	
Fine sand	Cattle slurry	BR	19	1995
		BA	38	
		INJ	50	
	Cattle slurry, aerated	BR	16	
	Cattle slurry, separated	BR	32	
Carex peat	Cattle slurry	BR	25	1996–1997
		BA	27	
		INJ	28	
	Cattle slurry, aerated	BR	23	
	Cattle slurry, separated	BR	22	

applied manure into the soil (Beauchamp et al. 1982, Cabrera and Vervoort 1998). Also, irrigation moistens soil, which enhances nitrification (Sierra et al. 2001) and thereby increases the mobility of manure N. On the other hand, increased moisture may also accelerate the immobilization of manure N (Flowers and Arnold 1983). Lindén et al. (1998) observed that the spring application method of pig slurry had a rather weak effect on spring barley yield and N recovery in a sandy soil, but incorporation appeared to enhance the effect of slurry in some cases. The difference between surface application and incorporation of slurry may be greater in a clay soil, into which slurry infiltrates less than into sandy soil (Bischoff 1984). However, the infiltration capacity of both clay and sandy soils varies according to the physical structure of the soil.

After incorporation by harrowing, manure is not completely covered by the soil, and some  $\text{NH}_3$  volatilization is possible (Sommer and Christensen 1990). Injection into the soil brings slurry deeper and covers it with soil more thoroughly. Greater immobilization may be another reason for lower N recovery after incorporation by harrowing than by injection (Paper III). Sørensen and Jensen (1995) and Sørensen and Amato (2002) observed greater immobilization and decreased plant uptake of slurry N after mixing slurry with soil than after injection, and suggested that the reason for the greater immobi-

Table 10. Apparent recovery of applied ammoniacal N of manures in the experiments with spring wheat and spring barley. BR = broadcasting, BA = band spreading, INJ = injection, INC = incorporation by harrowing.

Soil texture	Crop	Manure	Application time	Application technique	Apparent recovery of N, %	Years	Paper
Gyttja clay	Spring wheat	Pig slurry	Before sowing	BR + INC	12	1999	III
				BA + INC	12		
				INJ + INC	34		
Clay loam	Spring wheat	Pig slurry	Before sowing	BR + INC	12	1999–2000	
				BA + INC	14		
				INJ + INC	18		
		Pig slurry	1–2 leaf stage	BR	4.4		
				BA	7.6		
Clay loam	Spring wheat	Pig slurry	3–4 leaf stage	INJ	20	1999	
				BR	1.5		
				BA	0.6		
Clay loam	Spring barley	Pig slurry	Before sowing	INJ	2.3	1990–1993	IV
			After sowing	BR + INC	38		
		Pig peat manure	Before sowing	BR	17		
			After sowing	BR + INC	37		
				BR	27		

lization was the protection against predation that soil particles provided to microbes. When slurry is injected, the immobilizing microbes are mainly on the surface of the slurry without protection. Another reason for the greater immobilization of mixed slurry N may be that the slurry surface is greater, so that the slurry N is more available to microbes. Furthermore, the fixation of  $\text{NH}_4^+$  into clay minerals may be more extensive when mixing brings more slurry into contact with the soil (Scherer and Weimar, 1994).

As Kemppainen (1989) and Rees et al. (1993) observed, the injection of slurry on grassland increased the recovery of manure N through a higher N content of herbage compared with surface application (Paper II). However, grass growth is retarded by the negative effects of injection, such as physical damage to the plant canopy and roots (Hall 1986), the toxicity of some compounds in the slurry to plants and soil organisms (Hansen 1996, Tunney and Molloy 1986), and the lack of oxygen in the soil due to the decomposition of the organic compounds of the slurry (McAllister 1977).

When the barley yield was low because of the poor availability of N during the early growing season, the concentration of N in the yield was higher than in high yields (Paper IV). This somewhat levelled off the difference in the recovery of manure N. However, the N recovery in the yield was higher with methods and conditions that enhanced the uptake of N during early growth.

Manure applications should be timed so that manure N is available to the crop at the time of active N uptake. When slurry is spread to ley after the first cut, the available manure N is utilized in the growth of the second yield. For spring cereals, manure should be applied in spring before or right after sow-



ing, because cereals need N, especially in the earlier stages of growth. If application is delayed to the 3–4 leaf stage, earlier N demand must be met with an inorganic fertilizer.

The application of supplementary inorganic N fertilizer enhanced the growth of both cereals and ley (Papers II and IV) by providing readily available N at the very start of the growth. The improved early growth enables the crop to utilize more of the manure N that becomes available later during the growing season. Incorporation by harrowing mixes manure into the surface soil, but incorporated manure is not located as deep as inorganic fertilizer applied with a placement technique. Even if  $\text{NH}_3$  losses are prevented and manure N is within the reach of the plant roots, the initial immobilization of manure N into soil organic matter retards its uptake.

### **3.3 Effect of peat manure on soil moisture, organic carbon and aggregates**

#### **3.3.1 Soil moisture conditions**

When applied to a dry soil, peat manure or peat did not reduce soil drying in the spring. After irrigations and rain, however, peat or peat manure tended to limit soil moisture changes, especially when applied as a cover, or mulch, on the soil surface without incorporation. This is in accordance with the observations of Russel (1939) and Movahedi Naeini and Cook (2000): surface cover reduces evaporation only if the soil is moist up to the cover. Dry soil surface alone limits evaporation significantly (Idso et al. 1974), reducing the additional effect of the cover material. The effect of peat on soil moisture conditions has likely contributed to the result that, considering the effect of manure on grain yield, incorporation into the soil was more important for slurry than for peat manure (paper IV).

The effect was clearest in 1992, when irrigations were carried out during a long period of dry weather (Figure 5). The cover reduced the increase in soil moisture immediately after the irrigation and retarded drying of the soil later on. The first rainfalls after the irrigations on June 14–22, however, raised soil moisture more under the cover. Perhaps before the rain, more moisture remained in the covered soil than in the uncovered soil, even though the moisture contents measured before the rain at a depth of 15 cm were at the same level. Without rain or irrigation, the dry and hardened peat or peat manure layer formed a physical obstacle that hampered the early growth of barley sprouts.

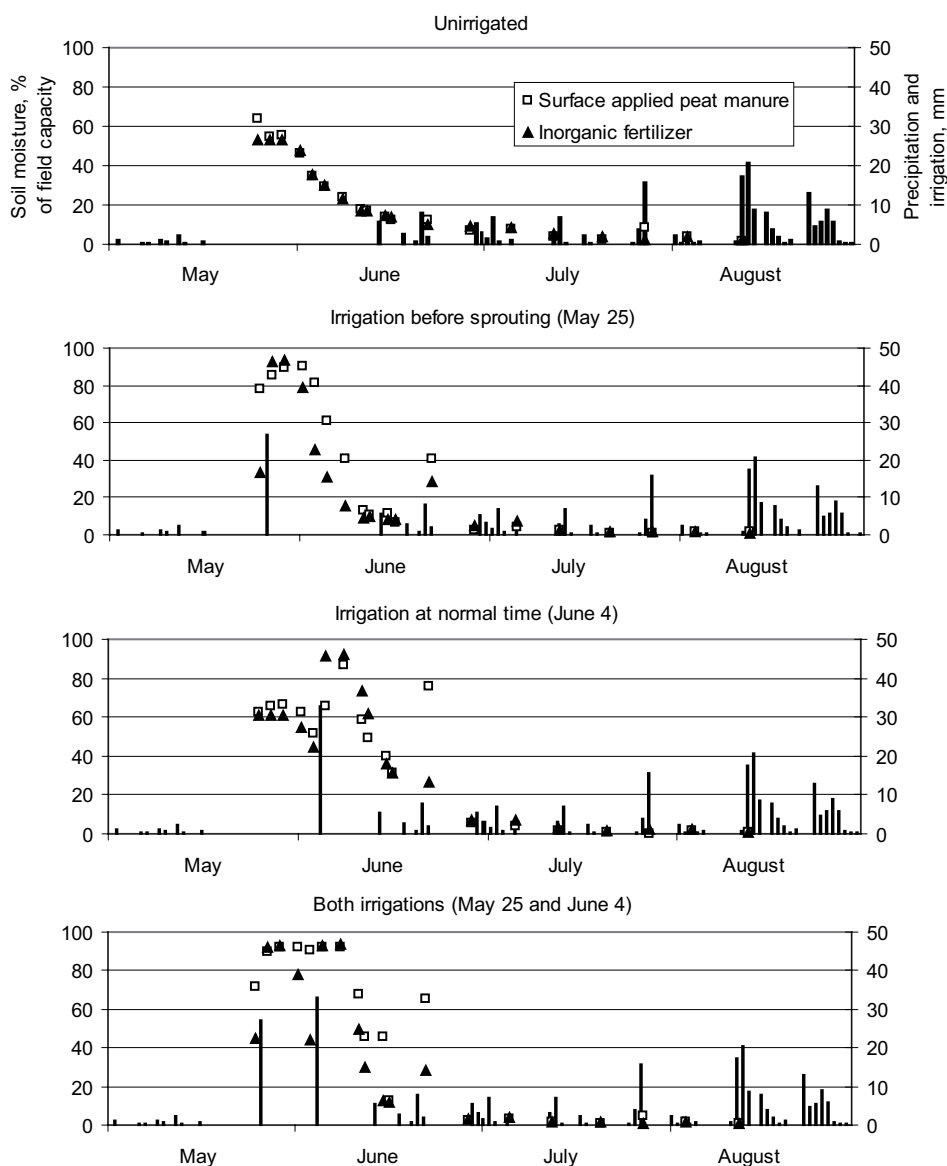


Figure 5. Soil moisture content as measured with gypsum blocks at a depth of 15 cm in 1992 in the plots treated with surface-applied peat manure or inorganic fertilizer drilled into the soil. Bars indicate the amount of water in precipitation and irrigation.

At each irrigation, about 30 mm of water was applied, which was sufficient to moisten both the peat cover and the surface layer of the soil. The peat may, however, totally absorb a smaller amount of precipitation, so that the water does not percolate into the soil and become available to the plant roots. For example,  $40 \text{ m}^3 \text{ ha}^{-1}$  of peat manure forms a 4-mm-thick layer, which has,

based on the water absorption capacity of peat (Verdonck et al. 1984), the potential to absorb almost 4 mm of precipitation. When *Sphagnum* peat dries, however, it changes from hydrophilic to hydrophobic (Michel et al. 2001), and its ability to absorb water diminishes: the more decomposed the peat, the greater its loss of absorption.

The experiment was performed on clay soil, where the upward capillary movement of water is slower and the risk of water deficit caused by peat manure cover is higher than with coarser soils. Gagnon et al. (1998) observed that peat manure or straw manure composts applied at high rates and incorporated to a depth of 10 cm depth increased soil moisture by 3–5%, especially in dry conditions in sandy loam, but not in clay (except in one case). The difference was considered dependent on the larger porosity or greater water-holding capacity of clay.

Peat manure cover may protect surface soil against slaking in heavy rain and alleviate subsequent crust formation upon drying (Johnston et al. 1997). In the experiment reported here, however, crust failed to form. Consequently, the possible protective effect of peat could not be assessed.

### **3.3.2 Soil organic carbon and aggregates**

With stubble mulch tillage, the concentration of organic carbon in surface soil (0–10 cm depth) after four annual manure applications was 20% higher in the plots that had received peat manure than in those plots treated with slurry (Figure 6). In ploughed plots, the difference between peat manure and slurry was small.

The aggregates of surface soil (0–10 cm depth) were fairly evenly distributed into the analysed size fractions (<2 mm, 2–6 mm and >6 mm): each fraction contained roughly 1/3 of the soil mass. In slurry plots the 2–6 mm fraction was 8% larger with ploughing than with stubble mulch tillage, but the other fractions showed no significant differences.

The average percentage of water-stable aggregates in the 2–6-mm fraction was 86% higher in stubble mulch tilled plots treated with peat manure than in stubble mulch tilled slurry plots (Figure 6). The corresponding difference in ploughed plots was 23%.

Increased organic carbon concentration and aggregate stability in the soil did not affect the grain yield of barley. The yields were about 3–4.5 Mg ha<sup>-1</sup> and there were no significant differences between the manure treatments.

The applied peat manure contained over six times as much organic matter as did slurry. This explains why peat manure increased soil organic carbon and aggregate stability more than did slurry. Repeated peat and manure applica-

tions added to the soil organic matter and improved the soil structure in other experiments, too (Persson and Kirchmann 1994, Gerzabek et al. 1995). Peat has a long lasting effect on the soil organic matter because it decomposes

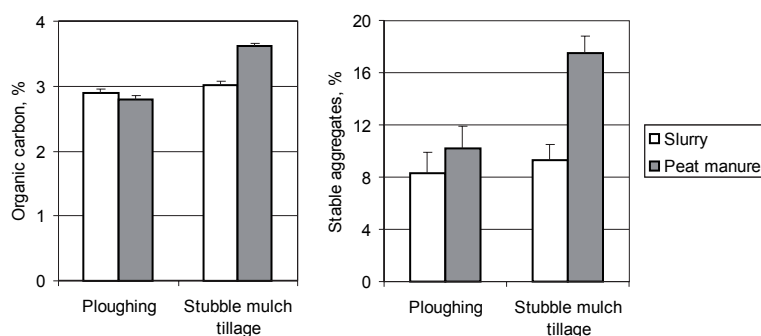


Figure 6. Organic carbon (% of dry matter) and stable soil aggregates (% of 2–6 mm size aggregate fraction dry matter) in soil at a depth of 0–10 cm in 1994 (residual effect). Tillage and manure treatments were applied in 1990–1993. Narrow bars indicate standard error of mean.

slowly (Persson and Kirchmann 1994). In an experiment by Pietola and Tanni (2003), however, the application of peat alone improved aggregate stability only slightly and temporarily. Stubble mulch tillage mixes the fresh organic matter of plant residues and manure into a smaller soil volume than does ploughing. Thus, the accumulation of organic matter in surface soil is faster with shallow tillage than with mouldboard ploughing, and results in greater stability of soil aggregates (Pietola and Tanni 2003).

In many previous studies, the application of manure and other organic materials also increased soil aggregate stability (e.g. Darwish et al. 1995, Gerzabek et al. 1995, Bissonnette et al. 2001). Increased stability renders the soil tillable in a higher moisture content and wider moisture range (Munkholm et al. 2002). However, the effect of manure may, on the one hand, strongly depend on its composition and application rate, and on the other hand, depend on the status of the soil receiving the manure. Manure does not always affect soil properties (Unger and Stewart 1974, Whalen and Chang 2002) or at least its effect on soil does not increase crop yields in all cases (Edmeades 2003), as was the case in the experiment reported here.

## 4 Conclusions

The injection of slurry into the soil, or its incorporation by harrowing, proved more efficient in reducing  $\text{NH}_3$  volatilization than did the surface application of slurry to a smaller area by band spreading or the reduction of the DM content of slurry by aeration or separation before surface application. The volatilization of  $\text{NH}_3$  was also low with surface-applied pig slurry on tilled bare

soil or in spring wheat stands in early stages of growth, apparently because the slurry infiltrated well into the surface soil.

Injection and incorporation also resulted in a higher recovery of manure N than with surface applications. Despite low  $\text{NH}_3$  losses, the N of slurry surface-applied to spring cereals was clearly less available than the N of injected or incorporated slurry. In dry conditions, which are common in Finland in spring, the ammoniacal N of surface-applied slurry was obviously adsorbed by the surface soil and remained mostly unavailable to plant roots.

The overall utilization of applied N could be increased by supplementing manures with inorganic fertilizer N, which provides crops with readily-available N at the start of their growth. The application of supplementary N is often reasonable to balance the ratio of N to phosphorus and potassium, as long as the total amount of applied N is not excessive.

The volatilization of  $\text{NH}_3$  from surface-applied peat manure was slow, but proceeded over a long time. Incorporation was not as important for the fertilizer effect of peat manure as it was for slurry, but both manures were more effective when incorporated.

Especially when applied to the soil surface, peat manure can help conserve soil moisture by reducing evaporation after the soil has been moistened by rain or irrigation. On the other hand, peat manure cover also retards the percolation of rain water into the soil, and thus keeps the soil dry when the amount of precipitation is low. Peat manure applications increase soil organic matter and aggregate stability. The accumulation of organic matter and stable aggregates in surface soil is faster with stubble mulch tillage than with mouldboard ploughing.

The results of the experiments presented here confirm that the injection in particular, as well as the incorporation of slurry effectively prevent  $\text{NH}_3$  losses and increase the utilization of manure N compared with surface application. The location of slurry and its nutrients in the soil after application with different techniques on varying soils requires more study, when estimating the fertilizer effect of manure.

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